Reversible decryption of covert nanometer-thick patterns in modular metamaterials

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Continuous development of security features is mandatory for the fight against forgery of valuable documents and products, the most notable example being banknotes. Such features demonstrate specific properties under certain stimuli such as fluorescent patterns glowing under ultraviolet light. These security features should also be hard to copy by unlicensed people and be interrogated by anyone using easily accessible tools. To this end, this Letter demonstrates the development of an ideal security feature enabled by the realization of modular metamaterials based on metal–dielectric—metal cavities that consist of two separate parts: metal nanoparticles on an elastomeric substrate and a bottom mirror coated with a thin dielectric. Patterns generated by creating nanometer-thick changes in the dielectric layer are invisible (encrypted) and can only be detected (decrypted) by sticking the elastomeric patch on. The observed optical effects such as visibility and colors can only be produced with the correct combination of materials and film thicknesses, making the proposed structures a strong alternative to compromised security features. © 2019 Optical Society of America

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Optical security features generate visual effects that are hard to imitate aiming authentication of original products [1]. Such features are ubiquitous and on many products of intellectual property, such as electronics, licensed merchandise, books, and valuable papers/documents. Banknotes use a number of optical security features some of which are fluorescent fibers embedded in paper glowing under ultraviolet light, watermarks appearing under certain illumination conditions, patterns changing colors with changing angle of view (iridescence), images created by infrared absorbing or reflecting prints [2,3]. Simultaneous use of these features improves the security of the product. As some of the features may be compromised over time, continuous development of new ones is a requirement to continue the anti-counterfeit efforts. Optical security features can also be designed for optical data encryption. Although, authentication and optical data encryption are typically used interchangeably in the literature, there is a critical difference between these two domains of applications: The information must be completely invisible in the encrypted state and be decrypted only with the right key for optical data encryption. Although, optical data encryption is less common than authentication; it is popularity increases as its need is anticipated to be inevitable in the near future with the ever-increasing computing power.

Most of the recently developed optical security features address both authentication and data encryption functions and take advantage of the advancements in the microfabrication techniques. A variety of optical phenomena are used for these reports including optical interference [4,5], plasmonics [6–12], photonic crystals [13–15], holograms [16,17], dielectric metasurfaces [18], luminescence [19], and Pauli blocking [20]. The encrypted patterns in these reports are created using optical or e-beam lithography [5–8,10,11,16–18], ultraviolet radiation [4,13], O2 plasma [14], laser scanning [9], printing on paper [20], stamping [12,13], and stenciling [5]. The patterns are then decrypted (or encrypted if they are decrypted as fabricated) by applying humidity [4,14], magnetic field [13], spectroscopic scanning [6], polarized laser light [9,16], exposure to O2/H2 gases [7,17], changing the refractive index of the medium [18], applying electrical signal [20], observing the thermal image [5,10,11]. Despite these successful demonstrations, the adaptation of these techniques into practice are limited mainly due to scaling issues associated with the low yield and the need for sophisticated equipment during microfabrication or decryption/encryption. A promising alternative is using metal–dielectric–metal optical cavities that eliminate the need for generating micro or nanoscale patterns and enable the use of the naked eye or camera to detect the patterns that are created by simply changing the dielectric thickness. Such an approach has been previously used for static color printing [21]. To adapt the optical
cavities for security applications, this study realizes dynamic (modular) optical cavities by transferring the top metal layer onto a separate transparent elastomeric substrate (patch) and encrypting the data as nanometer-thick patterns on the dielectric [Fig. 1]. Ultrathin top metal layers dewet the surfaces and form nanoparticles [22] creating metamaterials when they are stuck on the bottom part of the cavity. The novelty of this work is the realization of modular optical cavities using a scalable fabrication scheme and adapting them for convenient dynamic optical data encryption and authentication.

Fig. 1. Dynamic and reversible decryption of an encrypted star pattern generated by raising the SiO$_2$ layer by 10 nm (the SiO$_2$ thickness is 120 nm everywhere else) by sticking and removing a PDMS patch coated with Ag nanoparticles. The star pattern is 1 cm wide.

An optical cavity consists of a top absorber, e.g., a thin metal film, separated from a bottom mirror by a lossless dielectric layer. The optical response of such a cavity is determined by the optical properties and the thickness of each layer. For instance, an optical cavity consisting of 10 nm silver film as the absorber, 120 nm thick SiO$_2$ as the dielectric, and an optically thick (>80 nm) silver film as the mirror absorbs the red spectrum of the visible regime exhibiting blue surface color. A small increment in the dielectric thickness redshifts the reflection spectrum and creates a lighter blue surface color [Fig. 2(a)]. As a result, any pattern generated by changing the dielectric thickness is visible to the naked eye and cameras. Without the top absorber layer, however, the rest of the structure is an interference surface whose reflection spectrum is very similar to that of the bottom mirror [Fig. 2(b)], hiding (encrypting) the small change in the dielectric layer’s thickness. Decryption can be achieved by coating the absorber layer directly on the pattern. However, this method is inconvenient as it requires access to a deposition tool and it cannot be reversed. To enable convenient, dynamic, and reversible decryption we demonstrate using a transparent elastomeric substrate such as a polydimethylsiloxane (PDMS) patch that is precoated with the absorber layer. The patch is then stuck on the pattern for decryption and removed for re-encryption [Fig. 1]. While our decision of using PDMS as the elastomeric substrate is based on our experience with the material; it has recently enabled other modular optical applications such as enhanced fluorescent emission using Au-nanoparticles-coated-PDMS [23] and upconversion amplification by embedding lanthanide-doped nanocrystals in PDMS [24].

Fig. 2. Surface colors, cross section illustrations, and reflection spectra for (a) optical cavities consisting of 10 nm Ag (top) forming nanoparticles, 120 and 130 nm SiO$_2$ dielectric (middle), and optically thick Ag mirror (bottom) and (b) the same structure without the top Ag layer.

The optical cavities in Figure 1 and Figure 2 are based on 10 nm top Ag layer and 120 – 130 nm SiO$_2$ that are chosen after visualizing the color space that is attained by varying the thicknesses of the Ag and the dielectric layers. For the static cavities, 10 nm top Ag layer produces shades of blue as the SiO$_2$ thickness varies between 100 and 160 nm [Fig. 3(a)]. For increasing Ag thickness, the surface colors are richer but also fainter as the absorbance dip (resonance) sharpens [Fig. 3(b)]. Top-down scanning electron microscope (SEM) images of 10 nm Ag film show nanoparticles formation [Fig. 3(c), Fig. S1]. As a result, the optical response of the cavity with the
percolating top silver film exhibits a wider and deeper resonance compared to a simple cavity consisting of continuous and flat layers. The measured optical response is matched by the numerical simulations when the percolating behavior of the top Ag film is accounted for [Fig. S2].

The color contrast for the modular cavities is similar to that of the static ones for the top Ag thickness of 10 and 20 nm with slight shifts in the surface colors as a result of the refractive index of PDMS being larger than that of air [Fig. 4]. SEM images of the silver films on PDMS exhibit similar behavior to those on SiO2 surfaces explaining the similarity of the color spaces [Fig. S3]. However, the surface colors of the static and modular cavities for 30 nm Ag thickness do not match possibly due to the damages the silver film accumulates during repetitive sticking and removal of the patch [Fig. S4].

The color contrast for changing dielectric thickness is more crucial than the surface color itself for the proposed operation. Thus, the color contrasts for 10-nm-thick patterns are tested by varying the thicknesses of the top Ag film and the SiO2 layer. The results show clear color contrasts for the thickness range of 10 – 20 nm for Ag and 120 – 140 nm for SiO2 [Fig. S5]. Considering the observed contrasts and the robustness of the thin Ag films, the top Ag thickness is chosen as 10 nm for the following cases. While the pattern thickness for these cases is chosen as 10 nm as it is found sufficient for successful encryption and decryption; it is demonstrated that the patterns can be as thin as 2 nm to be successfully distinguished when decrypted [Fig. S6].

The optical data encryption relies on invisibility of the patterns without the PDMS patch and a noticeable color contrast with the patch on. Therefore, there is a lower limit on the pattern thickness to successfully decrypt the patterns and an upper limit to properly encrypt them. The upper limit strongly depends on the reflectance of the mirror layer and can be larger for higher reflectance. For instance, a perfect mirror with 100% reflectance would demonstrate the same performance with a lossless dielectric layer of any thickness on it. Thus, the patterns can have any thickness and still be invisible to the naked eye. For an actual metal mirror, however, the reflectance is lower than 100% and with a dielectric layer on top of the mirror, absorption of the incident light further increases as a result of enhanced interaction of the light and the
metal. In this case, a small change in the dielectric thickness can shift the reflection spectrum significantly enough to be noticed by the naked eye. For instance, while 10 nm thickness difference in the SiO$_2$ dielectric layer is completely invisible on a high-reflectance Ag layer; it can be noticed by the naked eye at certain angles of view and lighting conditions for an Ag layer with lower reflectance [Fig. S9]. Therefore, for proper encryption either high-reflectance metal mirrors should be used or patterns should be ultrathin at the expense of color contrast.

For the proposed function, an adhesion layer between the mirror layer and the substrate is necessary as without it the bottom mirror peels off the substrate while removing the PDMS patch. Just as importantly, PDMS patch should be fresh and be treated with O$_2$ plasma to increase the adhesion of the absorber layer. Without these precautions the absorber layer is partially transferred on surfaces upon sticking and removing the patch.

The optical cavities exhibit angle-dependent response as characterized by varying-angle spectroscopic measurements and also observed by the naked eye while changing the angle of view [Figs. S10, S11]. Although, the angle-dependent response is undesired for many applications such as color printing applications [25–27]: it is helpful for the proposed application as it enables finding an angle of view that maximizes the color contrast. Furthermore, patterns changing colors with the angle of view are the basis of many optical security (authentication) tags, stickers, and strips.

The final study is testing the endurance of a modular cavity by repeatedly sticking and removing the PDMS patch. Neither the PDMS patch nor the bottom part of the cavity shows any deterioration optically or mechanically after 200 cycles [Fig. S12]. However, it is observed that dust particles are captured in between the patch and the SiO$_2$ surface. Accumulation of such undesired particles may adversely affect the optical performance during the decryption operation, especially for patterns with high resolution. This limitation can be mitigated by keeping the surfaces clean at all times. Another limitation of the method is degradation of the top metal layer over time due to exposure to air. Possible solutions include using more resilient materials, e.g., Au, coating the metal layer with a thin barrier layer, and using metals that grow native oxide self-limiting the degradation process [22].

In summary, this study demonstrates the realization of modular optical cavities consisting of thin-Ag-coated PDMS patches and SiO$_2$-coated bottom mirrors. Patterns defined as nanometer-thick changes in the dielectric layer are encrypted without the PDMS patch and decrypted when the patch is stuck on the pattern, defining a new optical security modality. The proposed method can be employed for optical data encryption as well as security (authentication) features aiming anti-counterfeit applications.

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Supporting Information for

Reversible Decryption of Covert Nanometer-thick Patterns in Modular Metamaterials

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MATERIALS and METHODS

Fabrication: Ag films are deposited in a thermal evaporation chamber at $2 \times 10^{-6}$ Torr at a rate of $\sim 2$ Å/s. SiO$_2$ films are deposited in an e-beam evaporation chamber at $5 \times 10^{-5}$ Torr at a rate of $\sim 2$ Å/s. Some of the substrates are coated with 5 nm Ge film as an adhesion layer prior to coating the bottom Ag layer. PDMS is prepared with 1:10 ratio and is debubbled. PDMS surfaces are treated with O$_2$ plasma (100 W, 1 min) before the samples are put into the vacuum chamber for Ag coating.

Measurements: Varying angle spectroscopic measurements are performed using a visible wavelength ellipsometer (J.A. Woollam Co., V-Vase). Windows Pro 4 is used for recording the photographs and videos.

Simulations: The transfer-matrix method is used for cavities with flat layers. The refractive index of SiO$_2$ films is characterized using the ellipsometer (Figure S13). Palik data is used for modelling Ag layers. A FDTD software is used for the percolating Ag films. SEM images of the percolating films are processed and imported into the FDTD simulations.
Figure S1. Scanning electron microscope images of 10 nm, 20 nm, and 30 nm Ag films on SiO₂ films.
Figure S2. Simulation results. Solutions using the transfer-matrix method assuming perfectly flat layers (a) without and (b) with the top 10 nm Ag. (c) FDTD simulation results. Top shows the top-down view a small region of the percolating Ag film generated for the simulations using the SEM images (Dark regions are Ag). Bottom shows the simulated reflectance curves for 120 nm and 130 nm SiO₂. Each curve is the average of 9 simulations using different regions of the SEM image.
Figure S3. Scanning electron microscope images 10 nm, 20 nm, and 30 nm Ag films deposited on O$_2$-plasma-treated PDMS surfaces.
Figure S4. Photographs of 10-nm, 20-nm, and 30-nm-Ag-coated PDMS patches. Ag is on the top surface for the left column and at the bottom surface for the right.
Figure S5. Photographs of modular optical cavities revealing 10 nm SiO\textsubscript{2} patterns (squares or stars) for the indicated SiO\textsubscript{2} and top Ag thicknesses. Stars are 1 cm wide. Squares are 0.5 cm wide.
Figure S6. (a) Cross section illustration and (b) photograph a surface with square patterns generated by 8 nm, 6 nm, 4 nm, 2 nm, and 1 nm thickness difference in the SiO$_2$ layer. (c) Photograph of the surface upon forming the cavity. Square patterns are 0.5 cm wide.
Figure S7. (a-b) Photograph of the surface with the QR code pattern before and after sticking the PDMS patch on. (c) The contrast of the image is enhanced for QR scanners. The sample is 3 cm wide.
Figure S8. Al foil as the substrate and the bottom mirror. Cross section illustrations and photographs of the surfaces with and without the Ag-coated PDMS patch on.
Figure S9. Reflection spectra of SiO$_2$ on Ag mirrors with and without the Ge adhesion layer. The adhesion layer lowers the reflectance of the bare Ag mirror. The shift in the reflectance spectrum for 10 nm thickness difference in the SiO$_2$ layer is noticeably greater in (b).
Figure S10. Angle-dependent reflection spectra of a Ag (10 nm) – SiO$_2$ (120 nm) – Ag cavity. The absorbance dip weakens and blueshifts with increasing angle of incidence. Angle of incidence increases from 15° to 75° with 10° increments along the arrow direction for the plot.
Figure S11. Color space of the optical cavities at different angles of view. See Fig. 3 for cavity properties, i.e., top Ag and dielectric thicknesses.
Figure S12. Endurance tests. Photographs of the decrypted star pattern and 10-nm-Ag-coated PDMS patch after making and breaking the cavity the indicated number of times.
Figure S13. Measured refractive index of e-beam evaporated SiO$_2$ films.