Wide gamut, angle-insensitive structural colors based on deep-subwavelength bilayer media

Abstract: Wide gamut and angle-insensitive structural colors are highly desirable for many applications. Herein, a new type of lithography-free, planar bilayer nanostructures for generating structural colors is presented, which is basically composed of a deep-subwavelength, highly absorbing dielectric layer on an opaque metallic substrate. Experimental results show that a galaxy of brilliant structural colors can be generated by our structures, and which can cover $\sim 50\%$ of the standard red–green–blue color space by adjusting the nanostructure dimensions. The color appearances are robust with respect to the angle of vision. Theoretical partial reflected wave analyses reveal that the structural color effect is attributed to the strong optical asymmetric Fabry–Perot-type (F–P-type) thin-film resonance interference. The versatility of the structural color properties as well as the simplicity of their fabrication processes make this bilayer structures very promising for various applications, such as security marking, information encryption, and color display, etc.

Keywords: angle-insensitive; deep-subwavelength; lithography-free; structural colors; wide gamut.

1 Introduction

Colors play important roles in human life since they are capable of carrying information for people to distinguish objects and perceive the world [1–4]. In contrast to traditional colors generated from chemical dyes or pigments by the selective absorption and reflection of specific wavelengths of light, structural colors that arise from the interaction between light and nanostructures of objects rely strongly on the arrangement and shape of the nanostructures rather than their chemical properties, and have attracted great interest in recent decades due to their advantages of lower toxicity, superior stability, and higher anti-fading capacity [5–7]. During the past years, many types of optical engineering structures, such as, photonic crystals [8–12], metallic gratings [13], optical antennas [14, 15], plasmonic metamaterials, and metasurfaces [16–25], have been introduced to generate structural colors. While a wide gamut of color space can be covered based on such artificially engineered nanostructures, the realization of such nanostructures generally requires high precision micro-nano-fabrication techniques such as, electron-beam lithography [20, 21], nanoimprint lithography [22], focused ion beam milling [23], and direct laser writing [24], etc. This would result in high production cost and thus severely limiting their applications. Another strategy for generating structural color is based on planar thin-film stacks, including semiconductor-metal dual-layer [26–28], metal-insulator-metal triple-layer [29, 30], and multilayered structures [31–35]. Although such stratified media can be more easily realized in production and leading to the reduction of
processing costs, their performances are usually sensitive to the angle of vision [27, 30]. This feature is also unfavorable for some specific applications such as angle-independent displays and color filters.

In this paper, we propose and experimentally demonstrate a new type of cost-effective, lithography-free, planar bilayer nanostructures for generating vivid structural colors. The proposed devices basically consist of a deep-subwavelength, highly absorbing dielectric layer on an opaque metallic substrate. Here, Au is chosen as the optical metallic substrate, ascribed to the excellent chemical stability and the relatively lower ohmic losses than other metals. Copper oxide (CuO), as a highly absorbing medium at visible wavelength regime [36], is adopted as the top dielectric material. Experimental results show that the structural colors generated by our structures can cover ∼50 percent of the standard red–green–blue (sRGB) color space by adjusting the thickness of CuO layer, and display good angle-robust performance (the viewing angle is up to 80°), which exhibit obviously advanced performance than the results reported in the previous works that adopted the similar bilayer structures [27, 28]. Theoretical analyses not only confirm the experimental results, but also reveal that such structural color effect is attributed to the strong optical asymmetric Fabry–Perot-type (F–P-type) thin-film interference effects.

# 2 Experimental section

## 2.1 Samples fabrication

The fabrication procedure of the bilayer structure for producing structural colors is schematically illustrated in Figure 1A. Polished silicon (Si) wafers were first ultrasonically cleaned in sequence with acetone, alcohol, and deionized water (19.3 MΩ), followed by dried with nitrogen gas. A 150 nm gold (Au) layer was then deposited on the cleaned Si wafers by thermal evaporation (PZF-300, KYKY). In order to improve the adhesion between the Si wafer and Au film, a 10 nm chromium (Cr) film was deposited on the Si wafer before depositing the Au layer. Next, the gold-coated Si wafers were placed into the chamber of a high vacuum sputtering coater system (BAL-TEC, SCD 500) to grow a 5 nm thickness of copper (Cu) thin film. Then, a 3 nm thick Cu film was continued to grow by covering the first area of the sample with a mask. Through repeating the last step for several times by covering the deposited area with mask, at

![Figure 1: Fabrication process and characterization of the proposed bilayer thin-film nanostructures. (A) Schematic of the fabrication process of the proposed CuO/Au bilayer nanostructure. Surface and cross-sectional (insert) SEM images of a fabricated sample (B) before annealed (with 14 nm of Cu thin film) and (C) after annealed (with 30 nm of CuO thin film). XRD patterns of a structure consisting of a 50 nm thick Cu film deposited on Si substrate, before annealed (D) and after annealed (E).]
last, a series of thicknesses of Cu films (5, 8, 11, 14, and 17 nm) were obtained on a single substrate. After that, the ultrathin Cu films were annealing on a LED constant temperature heating table (SET-217) in air at 400°C for 2 h on a hot plate. As a result, the Cu thin films were oxidized to CuO thin films with the corresponding thickness of 12, 20, 26, 30, and 36 nm. Finally, a series of deep-subwavelength planar nanostructures with vivid structural colors were obtained.

2.2 Characterization

The morphologies of the fabricated samples were characterized by scanning electron microscope (SEM, FEI Sirion 200) at high-resolution mode. Figure 1B, C shows the surface/cross section SEM images of a fabricated sample before annealed (with 14 nm of Cu thin film) and after annealed (with 30 nm of CuO thin film), respectively. As one can see, after annealed at 400°C in ambient air for 2 h, well defined uniform artifacts with regular shapes are revealed on the surface of the sample (see Figure 1C and Figure S1 in Supplementary Material), indicating the existence of nanocrystallites.

To investigate the composition of the top nanolayer film, X-ray diffraction (XRD) measurements were performed (Bruker D8 ADVANCE). Figure 1D and Figure 1E shows the XRD patterns of a sample, which is composed of a 50 nm of Cu film deposited on Si substrate, before annealed and after annealed in the 2θ-scan range of 25° to 60°, respectively. As can be observed, the main phase of the sample before annealed is the Cu cubic phase with the (111) plane at the peak of 2θ = 43.59°. Another peak observed at 2θ = 50.75° is corresponding to the (200) plane. While after annealed, the XRD patterns exhibit two primary peaks (−111) and (111) phase of CuO at 2θ = 35.78° and 2θ = 38.94°, respectively, indicating that the Cu film was completely oxidized and transformed into CuO film.

The experimental reflection spectra were characterized using an angle resolved microscope (ARM, ideaoptics, China) for normal incident light and a UV–VIS-NIR spectrophotometer (Agilent Technologies, Cary 5000) for both s and p polarized light with allowed measured angle from 6° to 85°. The unpolarized reflection spectra were calculated through the formula: $R = (R_s + R_p)/2$.

3 Results and analysis

Figure 2A displays the experimental reflectance spectra for five different thickness of Cu thin films (5, 8, 11, 14, and 17 nm) deposited on Au at normal incidence. It is noted that for such intermediate structures there is no significant difference in the reflectance spectra, meaning that they can only cover a very limited range of color space. A photograph of these intermediate structures is shown in the top panel of Figure 6A, which was taken from an optical camera (Nikon, D7000). As expected, weak color changes are observed from this panel. Figure 2B shows the experimental reflectance spectra for five different thickness of CuO thin films (12, 20, 26, 30, and 36 nm) deposited on Au at normal incidence. Compared with Cu/Au intermediate structures, these CuO/Au samples possess completely different optical properties, all of them have much deeper and broader absorption resonances. More importantly, as the thickness of CuO increases, the resonance dip becomes redshift obviously. This makes our structures to probably generate different colors by modifying the reflection in a portion of the visible spectrum. The bottom panel of Figure 6A shows a photograph of these five fabricated samples. It is obvious that five distinct colors are really achieved: light yellow (12 nm of CuO), orange (20 nm), dark red (26 nm), dark purple (30 nm), and cyan (36 nm).

To gain insight into the characteristic of our structure, theoretical analyses were performed. We consider light incident from air ($N_1 = 1$) upon an absorbing film with thickness $h$ and complex refractive index $N_2 = n_2 + ik_2$, deposited on a metallic substrate with complex refractive index $N_m = n_m + ik_m$ at an angle $\theta$ (see Figure 3), according to Ref. [37], the reflection coefficient can be written as:

$$R = \frac{r_{12} + r_{21}e^{i\beta}}{1 + r_{12}r_{21}e^{i\beta}}$$

where $r_{1m}$ denotes the Fresnel reflection coefficient for light incident from medium $m$ to medium $n$ given by $r_{mn} = (N_m \cos \theta_m - N_n \cos \theta_n)/(N_m \cos \theta_m + N_n \cos \theta_n)$ for s polarized light and $r_{mn} = (N_n \cos \theta_m - N_m \cos \theta_n)/(N_n \cos \theta_m + N_m \cos \theta_n)$ for p polarized light, and $\beta = (2\pi/\lambda)N_m h \cos \theta_1$. The reflectance can thus be obtained by $R = |r|^2$. The calculated reflectance spectra corresponding to the measurements in Figure 2A, B are shown in Figure 2C, D, respectively. In our calculations, the refractive indices of Cu, CuO and Au were all taken from Ref. [38] (see Figure S2 in Supplementary Material). Note that the calculated spectra are coincident with the experimental results in all these cases. Especially, similar to Figure 2B, the large difference in reflectance is well reproduced in Figure 2D, this offers further evidence that in principle our structure can be used to generate different structural colors.

To provide further theoretical insights, we performed the partial reflected wave calculations to analyze the optical behaviors of our structures [39, 40]. As schematically shown in Figure 3, the reflection coefficient for such a
A coherent sum of the partial reflection waves, namely

$$r = \sum_{j=0}^{\infty} r_j$$

(2)

where $r_j$ denotes the roundtrip reflection coefficient and is given by

$$r_j = \begin{cases} 
  r_{12} & j = 0 \\
  t_{12}r_{1j}r_{j+1}t_{j+1}e^{2j\beta} & j \geq 1
\end{cases}$$

(3)

t_{mn}$ is the Fresnel transmission coefficient for light incident from medium $m$ to medium $n$ given by

$$t_{mn} = 2N_m \cos \theta_m / (N_m \cos \theta_m + N_n \cos \theta_n)$$

for $s$ polarized light, and

$$t_{mn} = 2N_m \cos \theta_m / (N_m \cos \theta_m + N_n \cos \theta_n)$$

for $p$ polarized light.

Figure 4 shows the complex phasor diagrams of the reflection coefficients for the structures studied in Figure 2B at the same wavelength of 555 nm, normal incidence. In the diagrams, each of partial reflected waves ($r_0$, $r_1$, $r_2$, ...) is displayed by phasors denoted as arrows and connected with one another sequentially in turn. The final coordinate of the phasor represents the total reflection ($R = |r|^2$) of the structure [41]. From Figure 4, we can see that at $h_{CuO} = 30$ nm (see Figure 4C), the amount of reflection returns to the closest point to the origin, that is, obtaining the strongest absorption. At other thicknesses, the reflections are all completely different: 46.5% ($h_{CuO} = 12$ nm), 14.4% ($h_{CuO} = 20$ nm), and 4.3% ($h_{CuO} = 36$ nm). The reflection values obtained here are in good agreement with the ones shown in Figure 2D at the same condition. Based on these results, we argue that: (i) the optical responses of our structures are related to the strong optical asymmetric F–P-type thin-film interference, and the high absorption property of the top layer, namely, the high imaginary part of the dielectric constant of CuO (see Figure S2, Supplementary Material). (ii) Our structure can indeed be used to produce vibrant structural colors.

The angular responses of the color effects of our structures are investigated. As we know, for conventional low-loss dielectric films, the optical response generally depends on the thickness of film and sensitive to the incident angle [8, 42]. Namely, their colors are sensitive to the angle of vision. While in the proposed bilayer system, there is little
phase accumulation even at higher oblique incident angles, since the thicknesses of CuO films are much smaller than the working wavelengths. Consequently, the optical response of our structures is insensitive to the incident angle. As a consequence, the colors of our structures would be robust with respect to the angle of vision (reflection angle).

Figure 4: The partial reflected wave calculations. Calculated partial reflected waves for different thicknesses of CuO films on an optical thick Au film. The wavelength ($\lambda = 555$ nm) and incidence angle ($\theta = 0^\circ$) are remain the same for the four complex phasor diagrams with $h_{CuO}$ equals to 12 nm (A), 20 nm (B), 30 nm (C), and 36 nm (D), respectively.

Figure 5A–C displays the experimental reflectance as a function of the wavelength and incident angle for s, p and unpolarized light, respectively. Here, $h_{CuO} = 30$ nm.

Figure 5: Angular responses of the optical reflection properties. Experimental (A, B, C) and calculated (D, E, F) reflectance spectra as a function of the wavelength and incident angle for s, p, and unpolarized light, respectively.
colors with wide gamut coverage. The displayed colors are robust with respect to the angle of vision. The calculated spectra are found to be in good agreement with the experimental results. Theoretical analyses discover that the physical mechanism of the structural color generation relies to the strong optical asymmetric F–P type thin-film resonance interference. To illustrate the functionality of the proposed device, a color image of a designed pattern based on our configuration was taken and is presented in Figure S3 (Supplementary Material). It is also worth mentioning that our structure holds potential for dynamic tunable color generation based on the reversible chemical conversion of CuO to copper sulfide (CuS) [45]. We anticipate that the lithography-free, wide-angle structural colors will open up new avenues for realizing relevant applications such as information storage, surface decoration and visual arts.

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