Ta/NiO subwavelength bilayer for wide gamut, strong interference structural color

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Abstract

In this paper we demonstrate that Ta/NiO bilayers may be use as high-efficiency, lithography free, reflective structural color filters for generating broad color gamut. Experimental results show that reflectance spectra present deep dips in the visible range, leading to strong structural colors that can be adjusted via the NiO subwavelength layer thickness. Simulation based on thin film interference theory allow to account for the experimental data. We demonstrate that the optical interference effect is still effective when the films are deposited on a flexible substrates such as paper and kapton, enabling to consider flexible color filtering applications.

1. Introduction

Selective interaction of light with matter (i.e. wavelength selection) results in colors due to physical processes such as absorption, reflection, refraction, scattering and interference. In a large number of cases, it involves interaction with electrons (i.e. transitions in band structures, orbitals...) [1]. Sometimes it may also arise from geometrical devices such as nano- and micro-structures. This is known as ‘structural color’. It produces a selective reflectance of the incident white light according to the nature and organization of the structure. This structural color has been responsible for brighter colors of living animals for million years [2] (i.e. for example the bright and iridescent blue color from Morpho butterfly wings [3]). In the last decades, inspired by the natural living, interaction of light with man-made artificial nano- and micro-structures have been intensively studied [4, 5]. Various technological approaches were used such as plasmon resonance from metal nanostructures, photonic crystals, diffraction from nanostructures arrays, optical resonance of metasurfaces and interference filters for generating broad color gamut. Experimental results show that reflectance spectra present deep dips in the visible range, leading to strong structural colors that can be adjusted via the NiO subwavelength layer thickness. Simulation based on thin film interference theory allow to account for the experimental data. We demonstrate that the optical interference effect is still effective when the films are deposited on a flexible substrates such as paper and kapton, enabling to consider flexible color filtering applications.

In this paper we propose and demonstrate high-efficiency, lithography free, reflective structural color filtering for generating wide color gamut. The proposed device structure is based on the low reflectivity metal Ta semi-infinite layer covered with a lossless dielectric nanometer-thick subwavelength NiO layer. NiO was chosen...
because among all the optical AR coatings involving different materials, NiO is rather overlooked [15, 17, 26–31] and little explored [32] despite the fact that NiO thin films have drawn much attention because their promising potential applications in solar or optoelectronic devices [33–41]. Moreover, because NiO may be considered as a lossless dielectric in the visible range, Ta was chosen because it is a metal with low reflectivity which is mandatory to induce a strong light absorption [16, 32]. Experimental results show that reflectance spectra present deep dips in the visible range, leading to strong structural colors that can be finely and continuously adjusted via the NiO layer thickness. Simulated curves based on thin film interference theory are in good agreement with the experimental curves. We demonstrate that this optical interference effect is still present when the films are deposited on flexible substrates such as paper or kapton.

2. Experiments

Commercially available Si/SiO₂ standard Silicon substrates were used to deposit two-layered Ta (50 nm)/NiO(NiO) structures. The Ta and NiO films where deposited using radio frequency (RF) magnetron sputtering from 3 inches targets. The Ta film was deposited under a power of 100 W and a pressure of 10⁻² mbar. The NiO films were deposited under a power of 50 W and a pressure of 6.10⁻³ mbar. With these sputtering conditions the growth rate for the Ta and for the NiO are respectively 0.138 nm s⁻¹ and 0.0395 nm s⁻¹. The nominal NiO thickness were \( t_{NiO} = 34, 50, 61, 97, 119, 154, 169 \) and 181 nm. Both layers where deposited without substrate heating. A sketch of the stack is presented on figure 1(a). Structural analysis of the Ta film alone and Ta/NiO films was carried out by X-Ray diffraction (XRD) analysis using CuK radiations \( \lambda = 1.54056 \) Å and presented on figure 1(b). The XRD peaks positions are typical of the one observed for polycrystalline Ta [42] and NiO [43, 44] films.

Reflectance spectra were obtained using a collimated light beam from a halogen white light source (Mikropack HL-2000 Ocean Optics), a 12 degree incident angle, and detecting the specular reflection with a 0.6 nm-resolution Vis/NIR spectrometer (SARSPEC, SpecRes+).

The measurements of the refractive indices of Ta and NiO were carried out in the optical region from 300 to 900 nm, at an angle of incidence of 70 degrees, using a Horiba (UVISEL) variable-angle ellipsometer. The measured ellipsometric angles \( \Delta \) and \( \Psi \) relate respectively to the amplitude ratio and to the phase difference between the complex reflection coefficients according to \( r^+ = \tan(\Psi)e^{i\Delta} \). The results were analyzed with a planar semi-infinite model for Ta and a multilayer model for NiO layers deposited on a Si substrate. The model consistency was verified for four different layer thicknesses.

3. Results and discussion

3.1. Reflectance spectra of Ta/NiO bilayers

Figure 2 displays the experimental unpolarized reflectance spectra for Ta/NiO thin films for nine increasing NiO layer thicknesses (0, 34, 50, 61, 97, 119, 154, 169 and 181 nm).

Clearly the uncoated Ta film has a weak reflectance across the visible spectrum (i.e. it increases from 40 percent to 60 percent). For every NiO thickness, the Ta/NiO bilayers show deep dips in the reflectance spectra. Increasing of the NiO thickness redshifts the resonance dips. It should be noted that for the lowest NiO thicknesses (i.e. 34, 50 and 61 nm) the reflectance spectra shows rather broad resonance compared to larger
thickness where the resonance is much sharper. Nevertheless, for the lowest NiO thicknesses a near-zero reflectance is still observed (from 1 to 3.8 percent of reflectance at the dip). Such values are comparable to the one obtained recently on Ni/NiO and Ti/TiO\[32\]. These sharp dips in the reflectance spectra create a wide variety of interference colors as presented for each NiO/Ta sample on figure 2.

### 3.2. Simulation of the reflectance spectra

The underlying mechanism for the creation of various colors can be explained in terms of multiple light reflections that occur at the film surface (here NiO) and the interface between the film and the non-perfect metallic substrate (here Ta) as sketched in figure 3(a)\[15,45\]. Complex refractive indices of the film and metallic substrate results in non trivial interface phase shifts, which can be modified by varying the degree of loss in the film and substrate\[13,15,16,46,47\]. Total phase accumulation includes both interface phase shifts and propagation in the film layer. Destructive interferences can thus be obtained at particular wavelengths depending on the sub-wavelength thickness of the film.

Let us consider light incident from air (N\(_1\) = 1) upon a slightly absorbing film (i.e. NiO) with thickness t and complex refractive index N\(_2\) = n\(_2\) + ik\(_2\) deposited on a metallic semi-infinite substrate with complex refractive index N\(_3\) = n\(_3\) + ik\(_3\) (i.e. Ta). The equations describing the reflective behavior of incident light on such a three layer structure are given by\[13\]:

\[
r = \frac{n_2 + r_{23} e^{2i\phi}}{1 + n_2 r_{23} e^{2i\phi}}
\]

where \(\phi = (2\pi/\lambda) t\) \(N_2 \cos(\theta_2)\) is the complex phase shift accumulated upon wave propagation in the NiO film and \(r_{ij}\) are the polarization-dependent Fresnel reflection coefficients for light refracted from medium i to j. These coefficients for s- and p-polarization are given by:

\[
r_{ij}^s = \frac{N_i \cos(\theta_i) - N_j \cos(\theta_j)}{N_i \cos(\theta_i) + N_j \cos(\theta_j)}
\]

\[
r_{ij}^p = \frac{N_i \cos(\theta_i) - N_j \cos(\theta_j)}{N_i \cos(\theta_i) + N_j \cos(\theta_j)}
\]

The angle \(\theta_i\) are related to the incidence angle \(\theta_1\) by Snell law, \(\theta_i = \sin^{-1}(N_1/N_i)\sin \theta_1\). Unpolarized light means an equal amount of power in the s and p polarizations, so that the effective reflectivity of the material is just the average of the two reflectivities:

\[
R = \frac{(R^s + R^p)}{2} \quad \text{with} \quad R^{s,p} = |r^{s,p}|^2
\]
The color of the reflected light is thus determined by the thickness of the NiO layer and the complex refractive indices of NiO and Ta.

The simulated reflectance spectra were generated under Matlab by computing equations (1) and (4) and the results are presented in figure 2 with the corresponding experimental reflectance spectra. In our simulations, the incident angle $\theta_1$ was set to 12 degrees. For each simulated reflectance spectra the NiO thickness was taken as the nominal deposited thickness. The refractive indices of Ta ($n_3, k_3$) and NiO ($n_2, k_2$) used for the simulation were those measured by variable-angle spectroscopic ellipsometry experiments that are displayed in figure 3.

The NiO dispersion curves are fairly flat in the visible range. The extinction coefficient $k_2$ is near zero for $500 < \lambda < 900$ nm and increases rapidly at $\lambda < 400$ nm due to electron interband excitation in the oxide. Indeed, NiO is a semiconductor with a direct band gap in the range of 3.0–4.0 eV as usually observed for sputtered nickel oxide thin films [48]. The refractive index is between 2.46 and 2.24 in the visible region. Both NiO refractive index ($n_2$) and extinction coefficient ($k_2$) dispersion curves are typical of NiO thin films [40, 49]. For tantalum, the refractive indices $n_3$ and $k_3$ respectively monotonously increase from 1.63 and 1.85 to 3.22 and 4.03 for $300 < \lambda < 900$ nm.

It should be noted that because NiO is a lossless dielectric in the visible range, light absorption principally occurs inside the metallic substrate [16].

Figure 2 compares the simulated reflective spectra (solid lines) to the experimental ones (dashed lines) and presents a good agreement between experiments and numerical predictions.

### 3.3. Color gamut

Each reflection spectra was transformed into CIE chromaticy coordinates $x$ and $y$ and was further converted to to sRGB values for display (detailed explanation for converting spectra to colors maybe found in several textbook [50] or papers [51]). Simulated sRGB colors deduced from the simulated reflectance spectra are presented in figure 2 and turn out to be in good accordance with the observed colors. In order to illustrate the variety of colors of our proposed structure, and to explore the color gamut, we have simulated color change in a wide range of NiO thicknesses. The results are presented in figure 4. Clearly a rich color palette may be obtained with NiO/Ta bilayers by varying the NiO thickness.

Flexible structural colors attract extensive interest owing to their potential optoelectronic applications. We have thus sputtered the NiO/Ta bilayers onto different flexible substrates: commercial Kapton® and commercial drawing paper. The flexible structural colored samples with different colors adhere perfectly onto these substrates. Figure 5 shows typical photographs for these flexible samples bent or not.
Because they are much thinner than the wavelength of light, ultrathin coatings have a low sensitivity to the angle of incidence. Indeed, with most of such coatings, the absorption features remain prominent for angle of incidence from 0 to 60 degrees as observed for lossy [15] or lossless dielectrics [16].

Due to the low angular sensitivity enabled by the sub-wavelength NiO layer thickness, the property of the flexible structural color remains almost unchanged when the colored membranes are bent. Furthermore, the fabrication technique of the flexible version of our color system is compatible with current micro-/nanofabrication industrial methods and has potential for large-scale production.

4. Conclusion

In this paper we have demonstrated that Ta/NiO bilayers may be use as high-efficiency, lithography free, reflective structural color filters for generating broad color gamut. Experimental results show that reflectance spectra present deep dips in the visible leading to strong structural colors that can be adjust via the NiO layer sub-
wavelength thickness. Simulated curves based on thin film interference effect well account for the measured reflectivity spectra. Moreover, we have shown that this optical interference effect is still present when the films are deposited on flexible substrates such as paper or kapton which makes these nanostructures widely applicable, and may be used for flexible color filtering devices.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Nassau K 1987 The fifteen causes of color: the physics and chemistry of color Color Res. Appl. 12 4
[2] Parcker A R 2000 515 million years of structural colour J. Opt. A: Pure Appl. Opt. 2 R15
[3] Zhang S and Chen Y 2015 Nanofabrication and coloration study of artificial morpho butterfly wings with aligned lamellae layers Sci. Rep. 5 1
[4] Zhao Y, Xie Z, Gu H, Zhe C and Gu Z 2012 Bio-inspired variable structural color materials Chem. Soc. Rev. 41 3297
[5] Shang L, Zhang W, Xu K and Zhao Y 2019 Bio-inspired intelligent structural color materials Mater. Horiz. 6 945
[6] Kristensen A, Yang J K W, Bozhevolnyi S I, Link S, Nordlander P, Halas N J and Mortensen N A 2017 Plasmonic colour generation Nature Reviews Materials 2 16088
[7] Shukat A, Noble F and Ari K M 2020 Nanostructured color filters: a review of recent developments Nanomaterials10 1554
[8] Ji C, Lee K-T, Xu T, Zhou J, Park H J and Guo L J 2017 Engineering light at the nanoscale: structural color filters and broadband perfect absorbers Adv. Opt. Mater. 5 1708368
[9] Xuan Z, Li J, Liu Q, Yi F, Wang S and Lu W 2021 Artificial structural colors and applications The Innovation 2 100081
[10] Yakovlev A V, Milichikov V A, Vinogradov V V and Vinogradov A V 2016 Inkjet color printing by interference nanostructures ACS Nano 10 3078
[11] Cheng F, Gao J, Liu T S and Yang X 2013 Structural color color printing based on plasmonic metamaterials of perfect light absorption Sci. Rep. 3 11045
[12] Park H J, Xu T, Lee J Y, Ledbetter A and Guo L J 2011 Photonic color filters integrated with organic solar cells for energy harvesting ACS Nano 5 7035
[13] Kats M A and Capasso F 2016 Optical absorbers based on strong interference in ultra-thin films Laser Photonics Rev. 10 735
[14] Fan W, Zeng J, Gan Q, Ji D, Song H, Liu W, Shi L and Wu L 2019 Iridescence-controlled and flexibly tunable retroreflective structural color film for smart displays Science Advances 5 eaaw8755
[15] Kats M A, Blanchard R, Genevet P and Capasso F 2013 Nanometre optical coatings based on strong interference effects in highly absorbing media Nat. Mater. 12 20
[16] ElKabbash M, Iram S, Letsou T, Hinczewski M and Strangi G 2018 Designer perfect light absorption using ultrathin lossless dielectrics on absorptive substrates Adv. Opt. Mater. 6 1806672
[17] Li Z, Butun S and Aydin K 2015 Large-Area, lithography-free super absorbers and color filters at visible frequencies using ultrathin metallic films ACS Photonics 2 183
[18] Yang C, Shen W, Zhang Y, Li K, Fang X, Zhang X and Liu X 2015a Compact multilayer film structure for angle insensitive color filtering Sci. Rep. 5 9285
[19] Kats M A and Capasso F 2014 Ultra-thin optical interference coatings on rough and flexible substrates Appl. Phys. Lett. 105 131108
[20] Park C-S and Lee S-S 2020 Narrowband and flexible perfect absorber based on a thin-film nano-resonator incorporating a dielectric overlay Sci. Rep. 10 17727
[21] Yu Y, Tang X, Huang G and Zhang P 2020 Large-area, flexible, full-color printings based on asymmetry fabry-perot cavity resonances Opt. Commun. 464 125483
[22] Zhao Z-J, Lee M, Kang H, Hwang S, Ieon S, Park N, Park S-H and Jeong J-H 2018 Eight inch wafer-scale flexible polarization-dependent color filters with ag-tio2 composite nanowires ACS Applied Materials & Interfaces 10 9188
[23] Lee K-T, Han S Y, Li Z, Baac H W and Park H J 2019 Flexible high-color-purity structural color filters based on a higher-order optical resonance suppression Sci. Rep. 9 14917
[24] Zhao J, Qiu M, Yu X, Yang X, Jin W, Le D and Yu Y 2019 Defining deep-subwavelength-resolution, wide-color-gamut, and large-viewing-angle flexible subtractive colors with an ultrathin asymmetric fabry-perot lossy cavity Adv. Opt. Mater. 7 1900646
[25] Chen F, Wang S-W, Liu X, Ji R, Yu L, Chen X and Lu W 2015 High performance colored selective absorbers for architecturally integrated solar applications J. Mater. Chem. A 3 7353
[26] Yang C, Shen W, Zhang Y, Li K, Fang X, Zhang X and Liu X 2015b Compact multilayer film structure for angle insensitive color filtering Sci. Rep. 5 9285
[27] Wang Z et al 2020 Towards full-colour tunability of inorganic electrochromic devices using ultracompact fabry-perot nanocavities Nat. Commun. 11 302
[28] Kim S, Kim S, Lee J, Jo Y, Seo Y-S, Lee M, Lee Y and Cho C R 2021 Color of copper/copper oxide Adv. Mater. 33 2007345
[29] Yang Z, Ji C, Liu D and Guo L J 2019 Enhancing the purity of reflective structural colors with ultrathin bilayer media as effective ideal absorbers Adv. Opt. Mater. 7 1900739
[30] Rana A S, Zubair M, Anwar M S, Saleem M and Mehmood M Q 2020 Engineering the absorption spectra of thin film multilayer absorbers for enhanced color purity in cmy color filters Opt. Mater. Express 10 268
[31] Tan J, Wu Z, Xu K, Meng Y, Lin G, Wang L and Wang Y 2020 Numerical study of an au-zno-al perfect absorber for a color filter with a high quality factor Plasmonics 15 293
[32] Letsou T, Elkabbash M, Iran S, Hinczewski M and Strangi G 2019 Heat-induced perfect light absorption in thin-film metasurfaces for structural coloring Opt. Mater. Express 9 1386
[33] Taeho M, Maestre D and Cremades A 2021 An approach to emerging optical and optoelectronic applications based on nio micro- and nanostructures Nanophotonics 10 1785
[34] Mistry B, Bhatt P, Bhavasar K, Trivedi S, Trivedi U and Joshi U 2011 Growth and properties of transparent p-NiO/n-ITO(In2o3:Sn) p-n junction thin film diode Thin Solid Films 519 3840
[35] Lee C-T, Chen C-C and Lee H-Y 2018a Three dimensional-stacked complementary thin-film transistors using n-type AlZnO and p-type NiO thin-film transistors Sci. Rep. 8 3968
[36] Qin P, Linder M, Brinck T, Boschloo G, Hagfeldt A and Sun L 2009 High incident photon-to-current conversion efficiency of p-type dye-sensitized solar cells based on nio and organic chromophores Adv. Mater. 21 2393
[37] Lee H, Huang Y-T, Horn M W and Feng S-P 2018b Engineered optical and electrical performance of rf-sputtered undoped nickel oxide thin films for inverted perovskite solar cells Sci. Rep. 8 5590
[38] Di Girolamo D, Di Giacomo F, Matteocci F, Marrani A G, Dini D and Abate A 2020 Progress, highlights and perspectives on nio in perovskite photovoltaics Chem. Sci. 11 7746
[39] Wahyuono R A et al 2021 Photocathodes beyond nio: charge transfer dynamics in a π-conjugated polymer functionalized with ru photosensitizers Sci. Rep. 11 2787
[40] Sun K et al 2015a Stable solar-driven oxidation of water by semiconducting photoanodes protected by transparent catalytic nickel oxide films PNAS 112 3612
[41] Sun K, McDowell M T, Nielander A C, Hu S, Shaner M R, Yang F, Brunschwig B S and Lewis N S 2015b Stable solar-driven water oxidation to o2(g) by ni-oxide-coated silicon photoanodes The Journal of Physical Chemistry Letters 6 592
[42] Navid A and Hodge A 2012 Nanostructured alpha and beta tantalum formationrelationship between plasma parameters and microstructure Materials Science and Engineering: A 536 49
[43] Chen H-L, Lu Y-M and Hwang W-S 2006 Thickness dependence of electrical and optical properties of sputtered nickel oxide films Thin Solid Films 514 361
[44] Dekadjevi D T, Suvorova A, Pogossian S, Spennato D and Ben Youssef J 2006 Experimental evidence for the role of nonuniform modes in the asymmetric magnetization reversal of a Ni/NiO system Phys. Rev. B 74 100402
[45] Pan H et al 2020 Wide gamut, angle-insensitive structural colors based on deep-subwavelength bilayer media Nanophotonics 9 3385
[46] Rensberg J et al 2017 Epsilon-near-zero substrate engineering for ultrathin-film perfect absorbers Physical Review Applied 8 014009
[47] Yu N and Capasso F 2014 Flat optics with designer metasurfaces Nat. Mater. 13 139
[48] Usha K S, Sivakumar R and Sanjeeviraja G 2013 Optical constants and dispersion energy parameters of nio thin films prepared by radio frequency magnetron sputtering technique J. Appl. Phys. 114 123501
[49] Al-Ghamdi A, Mahmoud W E, Yaghmour S and Al-Marzouki F 2009 Structure and optical properties of nanocrystalline nio thin film synthesized by sol-gel spin-coating method J. Alloys Compd. 486 9
[50] Schanda J (ed) 2007 Colorimetry: Understanding the CIE System (New York: Wiley)
[51] Chen Y et al 2020 Colored and paintable bilayer coatings with high solar-infrared reflectance for efficient cooling Science Advances 6 eaaz5413