

SPATIOTEMPORALLY RESOLVED DUAL BAND HYPERCHROMATIC STRUCTURAL COLOR USING A POROUS SILICON RUGATE FILTER

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SUMMARY

We introduce a novel scheme for achieving highly responsive structural color using dual band porous silicon rugate filters in conjunction with dual laser illumination. Spatiotemporally resolved sensing experiments are reported.

1. INTRODUCTION

Dynamic or responsive structural color devices present promising opportunities for emerging sensing and display technologies, with applications including point-of-care diagnostics, portable/wearable sensors, and low-power full-color displays¹. Moreover, colorimetric devices offer a more accessible and cost-effective alternative to bulky laboratory equipment for performing spatiotemporally resolved measurements. Instead of requiring expensive and challenging implementation, colorimetric devices only need a light source, sensor, and observation method. Attractively the observation could be realized with a smartphone, microscope camera, or the naked eye.

A significant challenge encountered by many responsive structural color devices is their limited ability to produce a large color response, dE , to slight changes in the input stimuli, dS . Our group has recently proposed a solution called "hyperchromatic structural color" to address this problem². HSC combines a responsive material system (e.g., porous silicon) characterized by a high spectral sensitivity $d\lambda/dS$, with an optical design characterized by strong colorimetric sensitivity $dE/d\lambda$ (e.g., multi-chromatic laser and an optical filter/sensor).

In this work, we demonstrate a dual band red-green laser illumination scheme paired with a dual band porous silicon rugate filter that exhibits highly chromatic and amplified structural color response (Fig. 1a-c). This design is shown to enable not only high sensitivity ($dE/d\lambda > 10 \text{ nm}^{-1}$), but also a wide dynamic range ($\sim 20 \text{ nm}$), and an ultra-fine equivalent measurement resolution ($< 0.1 \text{ nm}$). Knowledge of the device's baseline reflection spectrum combined with a numerical color model allows for a quantitative mapping between the observed color and the induced spectral response. As such, the measured chromaticity values (or hue) can be directly mapped to wavelength shift, and directly linked to the physical characteristics of the input stimuli (e.g., analyte concentration). We experimentally investigate and validate the spatiotemporally resolved performance of such devices in three illumination/observation formats: (1) specular projection onto a viewing screen, (2) direct viewing of scattered light, and (3) direct imaging in a microscope camera.

2. EXPERIMENTAL RESULTS

P-type $<100>$ silicon ($0.01\text{-}0.02 \text{ }\Omega\text{-cm}$) wafers were diced into $\sim 2 \times 2$ -inch pieces and anodized in $\sim 65 \text{ mL}$ of 15% ethanoic hydrofluoric acid solution. The dual band mesoporous silicon (pSi) rugate filter^{3,4} was realized using a current density $J(t)$ delivered by a Keithley 2601A with a waveform comprised of two cosine terms with frequencies 0.077 Hz and 0.1 Hz , with the min and max current densities set to 7.875 mA/cm^2 and 47.25 mA/cm^2 respectively. A total etch time near $\sim 1400 \text{ s}$ yields devices that are $\sim 25\text{-}30 \text{ }\mu\text{m}$ thick. Samples were oxidized at $T = 600^\circ\text{C}$ for 5 to 30 min in an ambient box furnace. The anodization recipe generates a refractive index profile approximately of the form: $n(z) = \delta n/4 [\cos(2\pi z/\Lambda_G) - \cos(2\pi z/\Lambda_R)] + n_{\text{avg}}$, where δn is the index contrast, Λ_G and Λ_R are the green and red Bragg periods, and n_{avg} is the average refractive index. For an optically lossy rugate filter comprised of lightly oxidized mesoporous silicon, we found this design can produce ideal sidelobe suppression and high extinction on the desired band edges without the apodization or quintic matching layers required in lower loss multi-layers (e.g., porous silica)³. Other combinations of $\pm \sin()$ and $\pm \cos()$ summations were found to yield less optimal spectral shapes. We further note that sidelobe suppression is critical to obtaining one-to-one mapping between the spectral shift and the induced color response, while the spectral sharpness of the band edges is inversely related to the dynamic range.

We characterized the optical and colorimetric response of the RG laser illuminated pSi rugate filters in three illumination/observation formats (noted above) across a variety of input refractive index stimuli including surface functionalization with small molecules, liquid capillary action, vapor adsorption, and aerosol microdroplet adsorption. In all cases, we observed highly responsive red-to-green color transitions which could be spatially monitored and quantified in real-time.

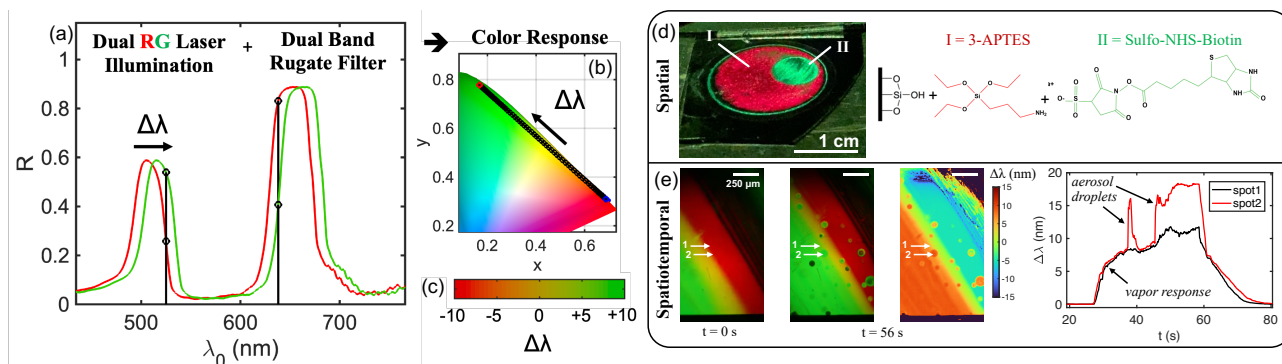


Figure 1: (a) Dual band pSi rugate filter reflectance spectra under perturbation from an input refractive index stimulus. Dual red/green laser illumination of the device enables a strong red-to-green color response as shown in: (b) CIE xy chromaticity space, and (c) the RGB color response. (d) Experimental demonstration of red-to-green color transition by surface functionalization, as photographed by a smartphone camera in a scattering configuration. (e) Experimental demonstration of spatiotemporal monitoring of isopropanol aerosol and vapor adsorption in a microscope configuration. As shown, the measured color response can be converted to wavelength shift.

Examples of spatially and spatiotemporally resolved structural color sensing are shown in Fig. 1d and Fig. 1e respectively. Although sensors were initially designed for specular projection viewing in accordance with prior work², we also observed strong wavelength and angle dependent optical scattering in our samples, which afforded the option of direct viewing without specular projection onto a viewing screen. Off-axis viewing of the red-to-green transition was facilitated by reducing the oxidation time, which effectively red-shifted the standard recipe. Consequently, the optimal laser/filter alignment depicted in Fig. 1a was not achieved at normal incidence but rather at an off-normal angle. In contrast, samples intended to undergo a red-to-green transition near normal incidence, like those in the microscope-integrated study illustrated in Fig. 1e, received the standard 30-minute oxidation treatment.

In the experiment shown in Fig. 1e, we use a microscope to observe a color gradient at the edge of a sample, where the applied current density $J(x,y,t)$ displays a significant local gradient across the x-y plane, creating a marked intrinsic color gradient. Speckle-free laser imaging is achieved using a customized low-cost microscope attachment and an agitated multimode fiber coupled to an RGB laser source with the blue channel disabled. We observed a strong color response to aerosols and vapors emanating from volatile organic compounds, such as isopropanol (IPA).

Initially, a sweeping shift in the background color is noted, aligning with the vapor deposition process. Subsequently, the interaction of aerosol microdroplets with the porous silicon surface is monitored in real time, capturing the adsorption and subsequent evaporation dynamics. Further studies reveal ~ 100 ppm IPA vapor concentrations induce ~ 2 -3 nm red shifts, which are readily monitored colorimetrically with an equivalent wavelength shift resolution near ~ 0.08 nm. Aside from the sensitive optical design, the fine resolution is also aided in part by (i) measuring signals in the chromaticity plane rather than along intensity axis, and (ii) averaging multiple pixels while discarding outlier pixels.

3. CONCLUSIONS

We have demonstrated dual band hyperchromatic structural color using a dual band pSi rugate filter combined with dichromatic laser illumination. Our approach achieves a superior color response compared to conventional white light illumination, while facilitating high dynamic range and high-resolution spatiotemporal sensing in a variety of low-cost illumination/observation formats. Quantitative imaging is enabled by a one-to-one mapping between the sensor's spectral shift and resulting chromaticity. Our findings indicate that pSi is highly effective for the creation of responsive colorimetric devices and represents a high performance and low-cost platform for the spatiotemporally precise analysis and measurement of dynamic processes involving nanoscale analytes.

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