Subwavelength Fano Resonant Porous Silicon Metasurfaces for Sensing and Dynamic Structural Color

Saddam Gafsi[1], Estevao Marques Dos Santos[1], Ivan Kravchenko[2], and Judson D. Ryckman[1,*]
[1]Holcombe Department of Electrical and Computer Engineering, Clemson University, Clemson, South Carolina, 29634, USA
[2]Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA
** jryckma@clemson.edu*

Abstract: We introduce the design, fabrication, and experimental investigation of subwavelength Fano resonant porous silicon metasurfaces functioning on the principle of guided mode resonance. These metasurfaces exhibit promise for dynamic structural coloration and sensing applications.
© 2024 The Author(s)

1. Introduction

Subwavelength-structured optical metasurfaces offer the potential to improve control over passive functionalities while also offering an attractive host platform for emerging types of dynamic metasurfaces and planar optics. In subwavelength and deep-subwavelength structured materials, an active material or analyte can have strong, intimate interactions with a localized near-field, surpassing the limitations of weak evanescent interaction. However, the development of subwavelength and deeply subwavelength metasurfaces remains challenging – especially at visible frequencies – owing to the demand for nanoscaled features.

Porous silicon (pSi) is an attractive sub-wavelength optical platform owing to its widely tunable optical properties, high surface area, and straight forward fabrication based on electrochemical anodization of silicon wafers. A wide variety of thin-film based pSi photonic components have been reported in the literature ranging from Fabry-Perot interferometers to Bragg mirrors, Rugate filters, and microcavities [1]. Such devices exploit the ability to modulate the refractive index n(z) in a bottom-up approach, primarily controlled through the variation of applied current density J(t) during fabrication. Integrating top-down device patterning methods either prior to or after anodization enhances control over light-matter interactions and the resulting device characteristics. Examples of pSi hybrid devices that synergize top-down and bottom-up fabrication techniques now include demonstrations of gratings, waveguides, ring resonators, micro-lenses, patterned Bragg reflectors, and volumetric optics [2]-[6].

Here, we introduce subwavelength Fano resonant pSi metasurfaces operating at visible wavelengths. As illustrated in Fig. 1(A-B), the devices are readily fabricated by electrochemical anodization of a pre-patterned silicon wafer. This allows for the introduction of deeply subwavelength features and mesopores (~20 – 50 nm diameter) without the need for ultra-high resolution patterning or conventional additive or subtractive processing techniques. Our structures exhibit highly tunable Fano resonances and operate based on the principles of guided mode resonance. Multiple design degrees of freedom are available, stemming from both the device geometry/patterning and electrochemical anodization parameters. This combination of top-down and bottom-up fabrication techniques is shown to provide an attractive pathway for the realization of high performance biosensors and dynamic structural color devices.

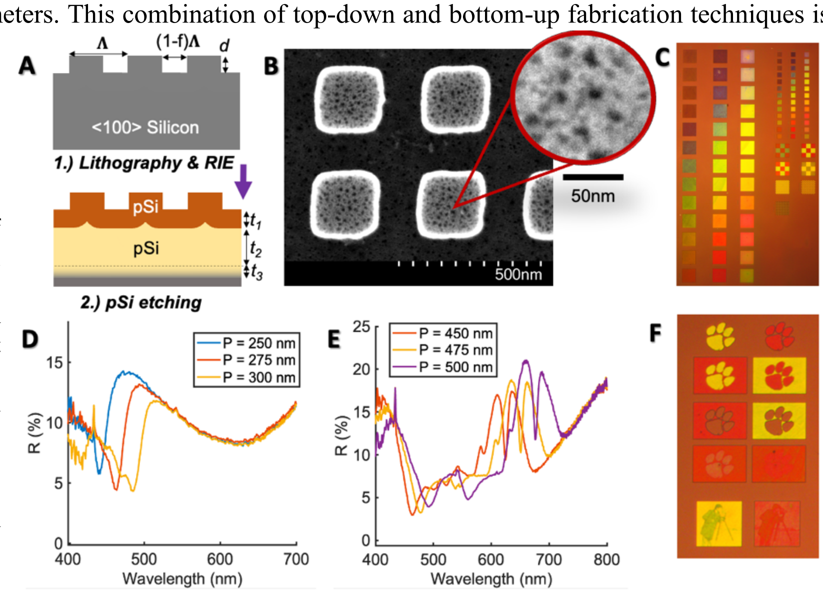

Figure 1. (A) Schematic of the fabrication process. (B) SEM images of a pSi meta-array. (C) Optical microscope image of the meta-arrays after anodization, showing vivid structural coloration under white light illumination. (D) Asymmetric and (E) symmetric Fano resonances observed in reflectance spectra for selected meta-arrays with varying periodicities. (F) Examples of structural coloration, including Clemson Tiger Paw and Camera Man test image.

2. Experimental Approach and Results

Our pSi metasurfaces (Fig. 1 a,b) were fabricated by first pre-patterning <100> silicon (0.01-0.02 Ω-cm) wafers via conventional top-down electron beam lithography (EBL) and reactive ion etching (RIE), followed by electrochemical anodization in 15% ethanoic hydrofluoric acid (HF) anodization with a computer controlled current density profile J(t). For visible wavelength resonance tailoring, an RIE etch depth of about ~200 nm was used, alongside meta-array periodicities in the range Λ = 200 – 500 nm. The current density recipe J(t) is comprised of three layers with controlled refractive index and porosity. The initial layer, featuring a higher refractive index and lower porosity, is formed by applying a current density of 25mA/cm² for approximately ~6 seconds, achieving a core layer thickness t_1 ~ 105 nm. Subsequently, the second layer, with a lower refractive index and higher porosity, is created using a current density of 47.2mA/cm² over a duration of roughly 3000 seconds, resulting in a substantial cladding layer of about 100μm. The third layer is prepared as a gradient index anti-reflection coating to suppress reflection from the silicon substrate using a half-cycle cosine pattern between 47.2 mA/cm² and 0 mA/cm². In our investigations, we also studied mesoporous silica devices oxidized in air at 800°C for a period ranging from 10 to 30 min. The outcomes of this fabrication process, along with Fano resonant spectra and vivid structural coloration under white light illumination are illustrated in Figure 1. As illustrated in Fig. 1d,e, spectra from two meta-arrays of a particular sample exhibit both asymmetric (Fig. 1d) and symmetric (Fig. 1e) Fano resonances, with wavelengths correlating to the local period Λ. The specific shape of the Fano resonance is influenced by multiple factors such as the optical thickness of the guiding layer, the depth of grating etch, and the resonance wavelength.

Lastly we extend beyond the passive spectral characteristics of the Fano resonant pSi metasurfaces and explore their reactive and dynamic behavior in response to refractive index changes. One particularly motivating objective is to deploy such devices for label-free biosensors, wherein the transduction mechanism is provided by a change in coloration. To enhance the color response, we illuminate the Fano resonant pSi metasurfaces with multi-chrome laser light rather than white light. The example shown in Fig. 2 demonstrates dynamic structural coloration triggered by water vapor adsorption. A dramatic cyan to red color change is observed for the meta-array best aligned with our cyan illumination wavelength ~495 nm. The results indicate pSi metasurfaces are a promising platform for dynamic structural coloration and biosensing applications.

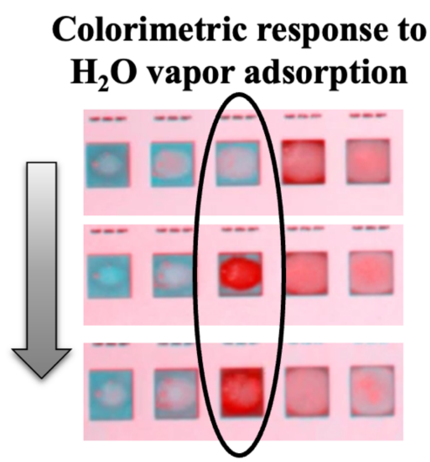

Figure 2. Dynamic structural color from a Fano resonant subwavelength pSi metasurface exposed to water vapor. Cyan/Red multi-chrome laser illumination is utilized rather than white light illumination.

3. Conclusion

To summarize, our research showcases the successful implementation of Fano resonant mesoporous silicon and silica metasurfaces that function within the visible light spectrum. We have explored their applicability in both static and dynamic structural color contexts. These devices are simple to fabricate and their resonant properties are highly customizable, owing to their multiple degrees of freedom provided by the combination of top-down patterning and bottom-up porosification methods. The capability of these metasurfaces to support normal incidence interrogation, colorful responses and confined interactions near the surface, positions them as a promising and adaptable platform for dynamic structural color applications and surface-based biosensing technologies.

Acknowledgements: This work was supported in part by the National Science Foundation under award #2047015 and the Air Force Office of Scientific Research (AFOSR) under award # FA9550-23-1-0448. This research was conducted as part of a user project at the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

References

[1] A. Jane, R. Dronov, A. Hodges, and N. H. Voelcker, *Trends in Biotech*. **2009**, 27(4), 230.
[2] X. Wei and S. M. Weiss, *Opt Express,* **2011**, 19(12), 11330.
[3] G. A. Rodriguez, S. R. Hu, and S. M. Weiss, *Opt Express,* **2015**, 23(6), 7111
[4] N. A. Krueger, et al. *Nano Lett*, **2016**, 16(12), 7402.
[5] D. Mangaiyarkarasi, et al., **2008**, *Opt Express*, 16(17), 12757.
[6] C. R. Ocier, et al., *Light Sci Appl*, **2020**, 9(196).
[7] T. H. Talukdar, B. McCoy, S. K. Timmins, T. Khan, and J. D. Ryckman, PNAS **2020**, 117(48) 30107-30117.