PAOO Based Hybrid Multilayers for Colorimetric and Interferometric Optical Sensing

Juris Prikulis[1], Uldis Malinovskis[1], Raimonds Poplausks[1], Aleksandrs Dutovs[1], Donats Erts[1]
[1]University of Latvia, Institute of Chemical Physics, Raiņa bulvāris 19, Riga, Latvia
juris.prikulis@lu.lv

Porous anodic aluminum oxide (PAAO) is a fascinating material, that can be grown into highly regular self-organized nanostructured layers using a variety of protocols [1]. The layer morphology (distance between pores, pore diameter, ranging from tenths to hundreds of nanometers) is generally determined by the choice of electrolyte and the anodization voltage, whereas layer thickness can be controlled by anodization time. PAAO synthesis is a very accessible method and can produce low-cost templates for the deposition of different other materials, creating new hybrid systems that can express multiple physical phenomena and simultaneously provide several useful functions for sensing. For instance, after deposition of a thin gold film on anodized aluminum surface one obtains a nanostructured Aluminum-PAAO-Gold (metal-insulator-metal, MIM) system which supports localized and propagating surface plasmon modes as well as Fabry–Pérot like resonances [2]. An alternative MIM structure was produced using capillary force assisted colloidal nanoparticle assembly on PAAO pore openings [3]. Another example of hybrid systems is a high-density array of photoluminescent ZnO nanorods that was synthesized in PAAO pores using atomic layer deposition (ALD) technique [4].

The obtained structures have a large exposed surface area, which can interact with the surrounding medium and is essential for high speed and high sensitivity devices. The presence of the analyte can conveniently be detected as a shift of resonance wavelength or change of the peak intensity using various optical configurations, such as extinction, reflection, photoluminescence (PL) or dark-field setups. However, a careful tuning of substrate geometry is required to benefit from the interplay of the different physical processes that can coexist in the hybrid multilayers. In particular, we demonstrate that PAAO layer thickness tuning can be used to maximize the signal intensity or refractometric sensitivity.

The PAAO layers were synthesized using two stage anodization protocol in 0.3 M oxalic acid electrolyte at 40 V potential difference. The process was modified to produce PAAO with a variable thickness on the same sample. During the second anodization both electrodes were simultaneously pulled out of the electrolyte solution [2]. Wedge-shaped PAAO layers on Aluminum surface with a thickness gradient ~100 nm/mm were obtained by the selection of the withdrawal speed ~5 mm/min. Thereafter the active sensor layer (ZnO for photoluminescence or Au nanostructures for plasmonic sensing) was deposited on the variable thickness PAAO template. The optical sensor setup was built on a standard fluorescence microscope with a Hg lamp light source and an imaging device (interferometric sensing) or fiber coupled to a spectrometer (colorimetric sensing). For MIM type substrates an S-polarized light source at a 60° incidence angle was used.

Several visible photoluminescence components, which correspond to different types of ZnO defects were identified upon illumination with UV light. By variation of PAAO layer thickness the intensity of individual components could be enhanced or suppressed. The intensity variation of any individual PL component correlated well with anti-reflective properties of ZnO NR–PAAO composite film at the peak wavelength of the particular PL component. This provides a route for selective enhancement or suppression of color components of hybrid fluorescent emitters by tuning only geometric parameters, with potential use in imaging and other optical devices. As an application example we tested the composite film for sensing of human proteins, specifically, vascular endothelial growth factor (VEGF). The intensity of the yellow and green PL components reduced in response to increased VEGF concentrations, whereas blue component remained invariant.

The two MIM type substrates showed similar behavior, namely, that the elastically scattered light upon angled illumination was maximized at specific PAAO thickness and wavelength combinations. In the case of Au film with nanoholes on PAAO, a distinct scattering maximum at $\lambda = 600$ nm vacuum wavelength occurred at 370 nm PAAO thicknesses. For the Au nanoparticle arrays similar effect was observed at $\lambda \approx 550$ nm and ≈ 350 nm PAAO thickness, but only for 60 nm, and 80 nm diameter and not 40 nm diameter particles. This gives a clear advantage for maximizing the signal to background ratio with the PAAO thickness in a narrow range between 300 nm and 375 nm. The best sensitivity expressed as the peak wavelength shift per refractive index unit (RIU) was found for 60 nm Au nanoparticles on 500 nm thick PAAO exceeding 200 nm/RIU.

For the interferometric detection the patterns in the recorded images were matched against refractive index changes. Similar to colorimetric setups, the sensitivity was improved at specific PAAO thickness.

In conclusion, variable thickness PAAO substrates have enabled performance optimization in several different multilayer architectures in various optical sensor configurations. Furthermore, the characterization and parameter tuning can be done using optical-only methods instead of analysis using electron microscopy. This makes the synthesis method easily reproducible and suitable for scalable production.

Funding: Latvian Council of Science fundamental and applied research project LZP-2020/1-0200.

[1] G. D. Sulka, “*Highly Ordered Anodic Porous Alumina Formation by Self-Organized Anodizing.*” In Nanostructured Materials in Electrochemistry, 1–116. Wiley-VCH Verlag GmbH & Co. KGaA, 2008.

[2] R. Poplausks, D. Jevdokimovs, U. Malinovskis, D. Erts, J. Prikulis. *ACS Omega* **3**, 5783–88 (2018).

[3] U. Malinovskis, R. Poplausks, D. Erts, K. Ramser, S. Tamulevičius, A. Tamulevičienė, Y. Gu, J. Prikulis. *Nanomaterials* **9**, 531. (2019)

[4] U. Malinovskis, A. Dutovs, R. Poplausks, D. Jevdokimovs, O. Graniel, M. Bechelany, I. Muiznieks, D. Erts, J. Prikulis. *Coatings* **11**, 756 (2021)