Variable Thickness Porous Anodic Alumina/Metal Film Bilayers for Optimization of Plasmonic Scattering by Nanoholes on Mirror

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ABSTRACT: Continuously variable thickness porous anodic aluminum oxide (PAAO) films were obtained using electrochemical oxidation of bulk aluminum sheet while both electrodes were simultaneously withdrawn from the electrolyte solution. The thickness gradient was controlled by the withdrawal rate (1–10 mm/min range) and thickness variation demonstrated from below 50 nm to above 1 micrometer. The thickness increased linearly with the sample lateral coordinate, whereas the nanopore structure (diameter and interpore distance) remained unchanged. Effects of the initial pore growth and capillary forces are discussed. The presented method can be used for tuning optimal PAAO thickness for optical and other applications as exemplified by finding maximum plasmonic scattering in structured Al−PAAO−Au multilayers. Enhanced scattering from porous gold film separated by a specific-thickness PAAO layer from aluminum mirror surface is demonstrated.

1. INTRODUCTION

Multilayer systems comprising of a reflective metal substrate, dielectric layer, and a layer of plasmonic nanostructures (nanoparticles or nanoholes in metal film) have recently attracted considerable attention1−10 for their potential applications including refractive index sensors, surface enhanced Raman scattering (SERS), anti-counterfeiting technology, color printing, or displays. The optical properties of such multilayers are governed by an interplay of structural Fabry−Pérot-like resonances, plasmonic effects, and near-field coupling between neighboring nanostructures. Additional functionality can be discovered if the dielectric layer contains cavities, such as pores in porous anodic aluminum oxide (PAAO) membranes. Resonators with open pores can for example be used for colorimetric detection of various molecules.11,12

Production of well-defined nanostructured layers typically employs lithographic methods, which are able to control the feature geometry in the two lateral dimensions. Studies of effects of structural variations in the third dimension often require production and characterization of many similar samples, which can be a tedious task and prohibitively expensive. The desired thickness range of dielectric layer in metal−insulator-nanostructured metal systems can vary from few nanometers for SERS applications6 to several micrometers for infrared resonators.7

In this work, we present a method for the production of continuously variable thickness PAAO films, which maintain their two-dimensional surface structure while the thickness can be tuned from approximately 50 nm to well above optical wavelengths on the same sample. The PAAO surface serves as a template for subsequent deposition of thin metal films with nanohole arrays, which show enhanced plasmonic scattering at specific PAAO thickness values.

The method is based on well-established anodization protocols of aluminum, which produce self-organized porous films, where pore diameters (tenths of nm) and center-to-center distance (tenths to hundreds of nm) can be selected by choice of electrolyte and anodizing potential.13 The desired thickness may be difficult to achieve due to initially unstable alumina growth phase,14 PAAO growth rate dependence on temperature,15 and often unknown crystallographic orientation of the underlying aluminum substrate.2 Here, we achieve variable thickness PAAO on the same sample by gradually terminating the oxidation by reducing electrolyte immersion depth during anodization in sulfuric and oxalic acid electrolytes.

As an application example of variable thickness, the PAAO membrane we demonstrate enhanced the plasmonic scattering from nanohole arrays in a thin Au film that are created by sputtering of Au on the PAAO surface. Plasmonic resonances in a sub-50 nm diameter holes in a thin gold film can be difficult to observe due to relatively small extinction cross section. In Al−PAAO−Au multilayers, plasmonic absorption can be noticed as subtle change in the reflection spectra.2,4 Here, we show that the resonant scattering from nanopores in gold film can be easily detected under angled illumination for specific values of PAAO thickness. This enables the application development based on a new plasmonic structure nanohole on mirror, which is a natural extension of the particle over mirror6 concept with the advantage that exceptionally dense nanohole arrays can be produced on a large scale using self-
organizing processes without a need of lithography or other sophisticated techniques.

2. RESULTS AND DISCUSSION

A number of samples were prepared using different pull-out speeds $V_{\text{sub}}$ using sulfuric and oxalic acid electrolytes. The sample regions with a deeper initial immersion are exposed to longer anodization times and consequently have a larger PAAO thickness. The top-view scanning electron microscopy (SEM) images (Figure 1) from regions near both ends (with significant thickness difference) of the sample reveal that pore diameters ($30-50$ nm for oxalic acid and $20-25$ nm for sulfuric acid electrolyte) remain constant throughout the sample. This result agrees with the observations during stationary pore growth using fixed electrodes where the pore size is determined by anodization voltage and electrolyte.$^{13}$ The above-mentioned diameter intervals account for local variations in pore size, shape, and measurement uncertainty.

Figure 2 shows the representative cross-sectional images of the oxalic-PAAO coated with a thin Au layer taken at different sample locations that correspond to different anodization times. One can observe that the pores below the outer layer are straight, with a constant diameter and at a local scale (nanometer to micrometer) resemble the structures of PAAO membranes obtained using fixed electrode anodization. To check the deposited Au film morphology, the film was transferred to poly(dimethylsiloxane) (PDMS) surface and Al-PAAO substrate removed by chemical etching. The resulting film has bumpy surface with holes (Figure 2d) that match the PAAO surface structure.

The obtained PAAO thickness grows linearly with lateral sample coordinate (regions with fitted lines in Figure 3), which correspond to stationary pore growth. However, deviations from the linear behavior are observed at the beginning of anodization, where pore growth is terminated before the establishment of stationary process. Further, the last, of approximately $2$ mm, has a nearly constant thickness because the anodization takes place in the meniscal region when the sample is practically above the electrolyte surface, yet the liquid bridge remains due to capillary effects. The anodization is terminated simultaneously in the entire meniscus area, when the capillary bridge eventually breaks.

The demonstrated PAAO thickness variations in $50$ nm to micrometer range on the same sample are of interest for optical applications. At higher withdrawal rates, tuning in sub-$50$ nm thickness range would be possible. At lower withdrawal rates or using longer electrodes, the thickness could be increased far above the optical wavelength scale. To better understand the PAAO thickness profile, one has to consider the kinetics of
current in electrodes that change their surface area during anodization (Figure 4). The process can be divided in three phases.

(i) In the initial phase, which is characterized by a high starting current that rapidly drops to a certain minimum and after ≈20–30 s recovers to a local maximum, the barrier layer is formed and pore formation starts. The kinetics of this phase is essentially identical to PAAO growth using a fixed-electrode setup.13,16 The process continues until eventually, the capillary bridge breaks and the current drops to zero. In this phase, the linear relation between anodization time and PAAO thickness is no longer valid because the ion flow is hindered by the confined meniscus volume.

(ii) In the steady phase, the current gradually decreases due to continuous electrode area reduction. In this phase, the film with the desired thickness gradient is formed. Although the PAAO thickness is determined by current density and process time, for practical purposes, it is of interest to estimate the PAAO thickness as a function of position on the sample. Assuming a constant PAAO growth rate \( V_g \) (typically 1.5–2 nm/s), the PAAO thickness increases linearly with anodization time \( t \) and sample lateral coordinate \( x = V_m t + b \), where \( b \) accounts for variation of immersion depth and uncertainty of meniscus shape at the initial stage. For a sample immersed about 14 mm deep and withdrawn at \( V_m = [1, \ldots, 5] \) mm/min, this results in ≈10 mm long zone with a continuous oxide growth.

(iii) In the final stage, the anodization takes place in the capillary meniscus region and is characterized by a faster reduction of anodization current. This process continues until eventually, the capillary bridge breaks and the current drops to zero. In this phase, the linear relation between anodization time and PAAO thickness is no longer valid because the ion flow is hindered by the confined meniscus volume.

Without the hexane layer (see Experimental Section), the electrolyte meniscus would rise several millimeters above the surface. In fact, this effect together with the impeded reaction rates at the upper (thinner) part of the meniscus can be used to obtain continuous gradient PAAO films in the 10–100 μm range. In our case, the meniscus formation is limited to ≈2 mm and sub-micrometer thickness gradient films are obtained by electrode withdrawal within few minutes. At the last millimeters of the sample (phase iii), the capillary forces modify the balance between the bulk electrolyte volume and the meniscus volume anodization and the linear PAAO thickness dependency on lateral coordinate no longer holds.

If the anodization would be performed during dipping rather than withdrawal, the meniscal region would continuously remain in the initial anodization phase, characterized by a high current density.18 However, this approach increases the risk of local breakdown, likely caused by inhomogeneities of the natural passivation layer that leads to local heating and uncontrolled oxidation.

In the reflected light, variable thickness Al-PAAO structures behave as expected and show a weak rainbow coloring caused by thin-film interference. The color saturation is significantly improved when PAAO is coated with a thin (semitransparent) layer of material with a substantially different dielectric permittivity, e.g., carbon19 or metal,20 a 20 nm Au film in the present study. Figure 5a shows the reflection spectra from selected locations with different PAAO thickness of an Au-coated oxalic-PAAO sample (photograph in Figure 5c). The spectral dependence of reflection on PAAO thickness (Figure 5d) is governed by the interference of partial reflections on all interfaces. The occasional spectral jumps in Figure 5d are most likely caused by grains of different crystallographic orientation of aluminum sheet,2 used for anodization. The majority of grains has (100) orientation20 and is characterized by higher oxidation reaction speeds (larger PAAO thickness) relative to the less frequent (110) or (111) oriented grains. Because the latter have a smaller PAAO thickness, they appear with blue-shifted response in comparison to the spectra of the surrounding dominant (100) grain. This could potentially be avoided using single-crystal aluminum substrates. One may also notice that the evolution of the reflection spectra with increasing lateral coordinate practically stops at the bottom of the sample, which can be explained by a slower anodization rate in the capillary meniscus of the electrolyte.

Plasmonic effects in nanostructured multilayers1,2,4 are relatively weak in comparison to interference coloring and often can escape unnoticed in reflection spectra (Figure 5a, d). An associated plasmonic phenomenon is resonant scattering, which can be observed using dark-field imaging setup. Localized surface plasmon resonances in the orange-red wavelength region are expected for gold films with a short-range ordered arrays of nanoholes1,2,22 and depend on the pore diameter and density. The scattering intensity spectra for porous gold films on different oxalic-PAAO layer thicknesses are shown in Figure 5b, f. Ignoring the noisy regions in the violet and infrared, there is a distinct scattering maximum at \( \lambda_0 = 600 \) nm vacuum wavelength occurring at 370 nm PAAO thicknesses. This is the key observation that demonstrates the method of thickness optimization for maximizing the scattering intensity. It would be very difficult to find this combination using a series of fixed-thickness samples. The resonant (enhanced) scattering in our case can also be seen by the naked eye when observing the sample at an angle that does not allow direct reflection from the light source (Figure 5e). Considering the effective refractive index \( n = 1.63 \) for PAAO,12 the 370 nm approximately equals the full wavelength \( \lambda_0/n \). Local maxima at \( \lambda_0 = 600 \) nm can also be noticed in Figure 5f for PAAO thickness of 250 nm and anticipated for thickness above 560 nm; however, a more accurate optical setup with well-defined incidence angle, polarization, detector linearity, etc. would be required to study these structures.

Figure 4. Typical current dynamics recorded during anodization with retracting electrodes from different electrolytes and withdrawal velocities. The intervals (i–iii) represent different phases of thickness-gradient anodization, see text.
symmetry and excess of subwavelength details, simulations of high-density (center separation below 100 nm) short-range ordered plasmonic nanohole arrays can be difficult. Even for less dense arrays, one has to resort to long-range ordering with periodic boundary conditions. A further complication is that the Au film is not flat and a grating-like coupling to electromagnetic radiation cannot be excluded. From the hexagonal arrangement of holes in the Au film, one may expect a strong angular dependency of coupling. However, the ordered domains are small (≈500 nm diameter; Figure 2), randomly oriented, and lack long-range periodicity.

3. CONCLUSIONS
A method of continuous thickness gradient nanostructured alumina film fabrication was presented. It can be applied to popular anodization protocols in sulfuric and oxalic acid electrolytes. We have demonstrated the applicability of the method for finding the optimal distance between the aluminum surface and the nanostructured gold film for maximizing plasmonic scattering. The developed method is perspective for further studies of dense plasmonic nanohole arrays on dielectric coatings of metals and may extend the concept of particle over mirror to nanohole over mirror with potential applications in plasmonic sensing, SERS, and solar energy harvesting.

4. EXPERIMENTAL SECTION
High-purity (99.999%) aluminum sheet (GoodFellow) with a thickness of 0.25 mm, cut in 9 × 18 mm² pieces, was used as the starting material for sample fabrication. After degreasing in acetone and isopropyl alcohol, the aluminum surface was electropolished for 3 min at room temperature in a mixture of 60% HClO₄ and C₂H₅OH (volumetric ratio 1:4) under applied voltage 10−15 V.<ref>

The first anodization was done using well-known two-step protocols either using 0.3 M H₂SO₄ at 20 V anodizing potential for 1 h or 0.3 M C₂H₂O₄ electrolyte with a 40 V anodizing voltage for 1 h. This was done at room temperature using aluminum anode and platinum cathode two-electrode cell. The oxide layer after first anodization stage was removed by a solution of H₃PO₄/CrO₃ (11:4%) at 70°C for 2 h.

The second anodization was done with the same conditions as in the first step, with the key difference that the electrodes were simultaneously pulled out from the solution at a 10−10 mm/min rate (Figure 6). A relatively large amount of electrolyte solution (>50 mL) was used to minimize the change in concentration and temperature. The anodizing
process was continuously monitored by recording the electric current and the immersion depth of the anode electrode. The basic idea is that the pore growth terminates in the sample region above the electrolyte surface. To reduce the capillary effects and meniscus formation, the electrolyte was covered with a 5 mm thick insulating and electrolyte repelling layer of hexane. The anodizing process was allowed to continue until the aluminum electrode plate was completely pulled out of the anodizing electrolyte. After that, the sample was washed with deionized water and dried at room temperature. The surface analysis of the porous anode was done using a scanning electron microscope (SEM, Hitachi 4800).

A 20 nm Au film was deposited on the Al-PAAO surface using the coating system (GATAN 682 PECS, Ar ion beam, 5 keV energy, 240 μA current, 0.8 Å/s, normal incidence, sample rotation 0.5 s⁻¹), resulting in a thin film with a dense array of 20–30 nm diameter holes.7 The reflection spectra were recorded using a fiber-coupled spectrometer (Ocean Optics USB4000) connected to an inverted microscope (Olympus IX71) with a 10× objective lens (Olympus CPLNFLN 10XPH, NA 0.3) and a standard microscope halogen lamp. The scattering spectra were recorded using the same setup, except a slide illumination from a fiber-coupled halogen light source (THORLABS OSL1-EC), 6.4 mm diameter aperture, placed at 30 degrees angle relative to the sample surface and 2 cm distance from the objective lens focus.

For a better SEM image contrast of the actual holes in the Au film, the film was transferred (facing upside down) to a PDMS (Sylgard 184 elastomer kit, Dow Corning) surface. After PDMS curing, the Al substrate was dissolved in a CuCl₂/FeCl₃ mixture.26 Finally, the PAAO was removed by a 5% H₃PO₄ solution at 70 °C for 1 h and washed with distilled water.

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was done within Latvian national research program IMIS 2 and Base/Performance Funding Project Nos. AAP2016/B043, ZD2010/AZ19. R.P. acknowledges support of ERDF project 1.1.1.2/16/I/001 application 1.1.1.2/VIAA/1/16/0184.

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