# In situ monitoring anodization of thin aluminum films with optical waveguide measurements

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**ABSTRACT** In the present work, we demonstrate the fabrication of an optical waveguide sensor, based on the bilayer of aluminum-porous alumina, by conducting optical measurements during the electrochemical anodization of thin aluminum films. In order to control the thickness of the aluminum layer required for optical waveguide measurements, we present a theoretical approach, which was verified experimentally, based on the angular dependent reflectivity spectrum of plasmon waveguide spectroscopy under the Kretschmann configuration.

## INTRODUCTION:

The field of plasmonics forms a major part of the fascinating area of nanotechnology, which deals with the electromagnetic fields and the confinement over dimensions on the order of or smaller of than the wavelength. Plasmon excitation is based on interaction processes between electromagnetic radiation and conduction electrons in metallic interfaces or in small metallic nanostructures [1]. In the recent years, a wide variety of applications [2], which have been already demonstrated or hold promise for the future, include chemical and biological sensors, near field microscopy, surface-enhanced Raman spectroscopy, nonlinear optics, heat assisted magnetic recording, nanophotonics, cancer detection and treatment. Surface plasmon resonance (SPR) is an extremely sensitive function of the surrounding dielectric index. This fact accounts for the extended impact of surface plasmons on chemical and biological sensors. Surface plasmon sensors were first proposed by Nylander *et al.* in 1982 for sensing the presence of trace amounts of various gases [3] and since then they are considered to be of great scientific interest. Under certain conditions, they may offer real-time, in situ, nondestructive analysis of dynamic surface events and thus is capable of determining rates of adsorption and desorption for a range of interfacial processes. The SPR technique has been used for in situ adsorption studies of self-assembled monolayers (SAM) [4], polymer adsorption on metal or chemically altered surfaces [5] and in many biological applications such as protein interactions, lipid bilayers, tissue engineering, cell adhesion on biomaterial surfaces, and antigen–antibody binding [6]. However sensors based on interactions at planar surfaces have a certain detection limit. In order to overcome this limitation coupled plasmon waveguide spectroscopy which makes use of porous media has been proposed [7].

Porous anodic alumina (PAA) holds a prominent position among nanostructured porous media used for sensing purposes. The development of electron microscopy at 1950's revealed that the anodization of high purity aluminum foils in acidic solutions results in the formation of self-ordered hexagonal arrays of cells containing cylindrical pores extending perpendicular to the surface. The dependence of the PAA morphology on anodization parameters has been investigated experimentally in several studies [8]. It was not until 1995 that Masuda *et al.* [9] introduced the two step anodization which increases the periodicity of the pores dramatically. In contrast to aluminum membranes, foils etc, thin aluminum films are not considered suitable for the two-step anodization due to their thickness. Several studies have been introduced revealing the properties of thin aluminum film anodization [10]. In the present work, our research is concerned with the fabrication of a plasmon-based aluminum-porous anodic alumina sensor. The later bilayer consists of a plasmonic aluminum layer of 15 nm and porous alumina adlayer resulted from the partial anodization of aluminum film deposited on glass substrate.

Our quantitative method is based on the theoretical behavior of reflectivity curves for films with equal aluminum thickness and different porous-alumina thicknesses comparing to a sample with bare aluminum film. As depicted in fig.1, reflectivity curves for samples with equal thickness of aluminum and different thickness of PAA intersect at an adequately small range of incident angles. Furthermore the slope of the curves in a wide range of incident angles, indicate that the reflectivity of samples with equal aluminum thickness could be considered experimentally identical.

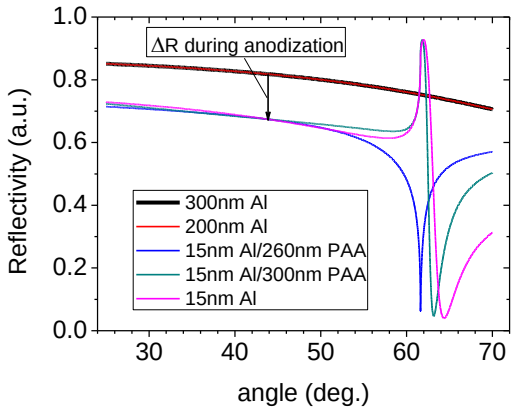


Fig.1 Theoretical reflectivity curves for five different systems. Curves that depict 200nm Al and 300nm Al are identical.

## EXPERIMENTAL METHODS:

Equilateral BK7 prisms with refractive index n=1.515 (λ=632.8nm) were used to excite optical wavequide modes under Kretschmann configuration. Square glasses (Corning 7059) were cut in smaller pieces (20x30x1 $mm^3$) and used as substrates. The glass substrates were immersed in sulfochromic acid for 2 hours, rinsed with deionized water, ethanol and finally dried in nitrogen gas stream. Identical procedure was adopted for cleaning the prisms. Cedar wood oil (P/N 251001, PanReac Applichem) was used as refractive index matching liquid between the prism and the glass substrate. An aluminum film of about 215 nm was deposited on three glass substrates via thermal vapor deposition technique, under base pressure of $1x10^{-6}$ Torr with a rate of 0.3 nm /sec. The rate was monitored by an

oscillating quartz crystal. Under the same conditions we prepared an aluminium film of 15 nm which was used as a reference sample. Optical measurements were performed in our laboratory surface plasmon resonance apparatus described in previous work [11]. Electrochemical anodization of aluminium films was carried out at a custom-build cell made of PMMA which was placed in contact with the system prism/glass substrate/aluminium film. A gold wire in the form of a coil was used as a counter electrode. The samples were partially anodized in 0.3M sulphuric acid aqueous solution under constant voltage of 20V at room temperature. The angle of incidence, during anodization of each sample, was fixed in the vicinity of the intersection range ($44.2^{o}$) and the moment of cutting off the applied voltage was decided according to the reflectivity of the reference sample (aluminum-15 nm) at the same angle. The characteristic current vs time and reflectivity vs time curves were monitored simultaneously.

**RESULTS AND DISCUSSION**:

The following diagram (fig.2) depict the experimental curves of reflectivity at constant angle during the anodization of (3) samples.

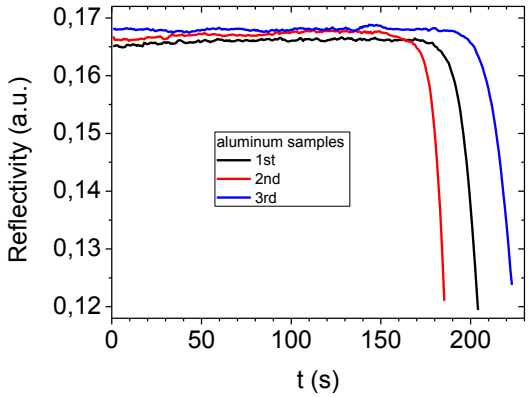


Fig.2 Reflectivity vs time monitored in situ during anodization of 3 samples.

The reflectivity vs time is constant for thicknesses that exceed the optimum plasmonic thickness (15 nm for aluminum). The decrease of the reflectivity during the last seconds of the process implies that the thickness of the remaining aluminum is less than 50nm. The appropriate moment during the anodization process at which the desired aluminum thickness has been acquired, is determined by a single measurement of the reference sample. The reference reflectivity value at which the anodization process was stopped is 0.124mV as depicted in fig.2.

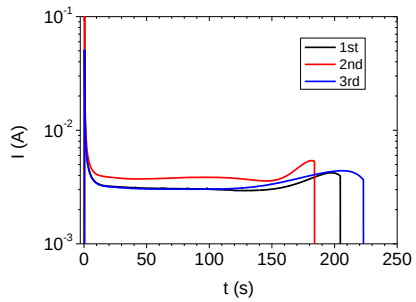


Fig.3 Characteristic current vs time curves of the anodization of thin aluminum films at 0.3M sulphuric acid under applied voltage of 20V at room temperature.

The respective current vs time curves of anodization for the three samples are presented in the diagram of fig.3. Within several seconds from the onset of the anodization, the current reaches a constant value, indicating that the aluminum oxide growth rate is stable over time.

In order to verify the potential use of the partially anodized samples as optical sensors, we demonstrate (fig. 4) the waveguide optical mode excited in contact with water (black curve) and 8.35% w/w ethanol aqueous solution (red curve). The shift is caused by the increase of the effective dielectric constant due to the presence of ethanol. The adsorption of various molecules in PAA could be quantified by monitoring the shift in the minimum of the reflectivity curve.

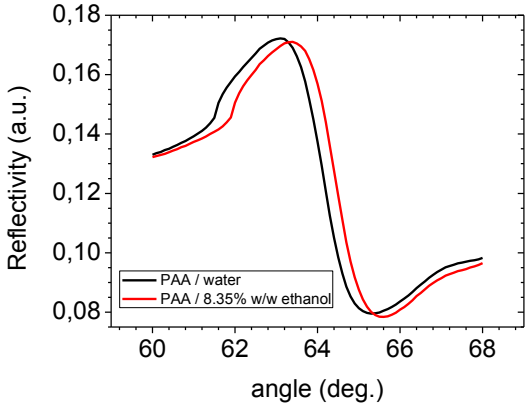


Fig.4 Experimental reflectivity for the system aluminum/porous anodic alumina in contact with water (black curve) and 8.35% w/w ethanol aqueous solution (red curve) respectively.

Furthermore by fitting the reflectivity vs time curves the consumption rates of aluminum during anodization can be calculated for different acidic solutions and concentrations.

**CONCLUSIONS:**

The theoretical approach for monitoring the anodization of thin aluminum films by conducting optical measurements was experimentally verified. This method could be adopted for the fabrication of optical sensors based on the bilayer aluminum/porous alumina.

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