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ScienceDirect
Colloids and Surfaces B: Biointerfaces 56 (2007) 163–169
COLLOIDS AND SURFACES B
www.elsevier.com/locate/colsurfb

In-situ monitoring of the dielectric and electrostrictive properties of anodised thin films for biochip applications

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Available online 27 October 2006

Abstract

Further improving the performance of capacitance-based DNA microsensors will depend on the ability to synthesize simply, at a low cost, thin films of high dielectric permittivity with a well-controlled growth morphology. Anodisation of the valve metals Ti, Zr and Ta is a promising route for preparing such films. In this paper, we propose a new method for following the evolution of the dielectric properties of such anodised metallic oxide thin films in-situ during their growth. The technique relies on measuring the evolution of the electrostatic stress developing in the film. Measurements have been carried out on anodic TiO_2 films grown galvanostatically in HNO_3 at 1 and 3 mA/cm^2 and in H_3PO_4 at 0.5 mA/cm^2. The dielectric permittivity of the films was observed to decrease during the initial stage of anodisation, characterised by a steady increase of the cell voltage with time. The permittivity then reached a constant value when the oxide entered a second growth regime, characterised by a stabilisation of the cell voltage. The origin of the observed permittivity evolution is interpreted in terms of the evolution of the growth morphology of the films during anodisation.

Keywords: Dielectric permittivity; Electrostriction; Anodising; Integrated biosensors

1. Introduction

The main challenge associated with biochips is the capability for fast electrical detection of very small DNA amounts. Sensors of the last generation can achieve DNA detection in the nanomolar range. However, the need for detection of smaller quantities urges for further lowering the detection threshold of the sensors. Sensing methods usually rely on the measurement of combined resistance and capacitance changes induced by DNA hybridization on the sensor surface. An example of the latter type of sensor was developed by Moreno-Hagelsieb et al. [1]. They designed a sensor based on interdigitated micro-electrodes and an Al_2O_3 film as the dielectric layer. The detection threshold of such a sensor was shown to be directly related to the permittivity of the dielectric layer. Replacing alumina with another oxide of larger dielectric constant thus offers a straightforward strategy for further increasing the sensitivity of the sensor. In this respect, TiO_2, with its dielectric permittivity as high as 100 for dense well-crystallised material [2], is a promising candidate. Dense crystalline TiO_2 films can be obtained by anodisation of Ti surfaces under optimised conditions, anodising being a relatively straightforward technique, which is compatible with integrated biosensor fabrication. However, the characteristics of the oxide films formed are sensitive to the processing conditions. Therefore a good control of the anodising process is crucial. In previous work, we have monitored the anodising process of such TiO_2 films in-situ by means of continuous high-resolution substrate curvature measurements, carried out with a multi-beam laser technique [3]. In the present paper, we demonstrate the use that can be made of such in-situ curvature measurements for characterising the evolution of the dielectric properties of the oxide film during anodisation.

The dielectric properties of the oxide were determined by measuring the electrostatic stress developing in the thin film. The electrostatic stress (σ^{ES}) actually encompasses two distinct contributions: the Maxwell stress and electrostriction. The former is the compressive stress arising from the coulombic attraction between the positive and negative charges located on opposite sides of a dielectric. Electrostriction can be defined as the second order coupling between strains and the electrostatic field. When a dielectric material is submitted to an electrical field, it experiences a Maxwell stress. Then, due to the action of the coulombic force, the dielectric tends to contract. This strain will provoke in turn a modification of the dielectric constant of the material

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doi:10.1016/j.colsurfb.2006.10.021

(electrostriction) and therefore of the magnitude of the Maxwell stress as well. The two stress components are thus coupled and cannot be treated independently. Electrostrictive coefficients of bulk materials are classically determined either by applying an oscillating electric field to the dielectric and measuring the resulting strain (direct effect), or by applying a mechanical load to the sample and measuring the change of the dielectric permittivity of the material (converse effect) [4]. In contrast, measuring electrostrictive properties of thin films is usually challenging due to the risk of damaging the film and the difficulty of controlling the boundary conditions [5]. Therefore, in the case of thin films, the use of alternative techniques is mandatory, allowing for loading and probing the material without any direct contact. The membrane method described by Wüthrich [6] or the ellipsometric one proposed by Ord [7] are good examples of techniques adapted for measuring the electrostatic properties of oxide thin films.

Our own experimental setup, developed originally for monitoring of growth stresses developing in thin films [8], offers an alternative technique, based on in-situ high-resolution substrate curvature measurements. It turned out to be particularly well-adapted for measuring the evolution of the electrostatic properties of anodised thin films. Indeed, as the dielectric film grows on a rigid cantilevered substrate, the boundary conditions are well-controlled. In addition, the curvature of the samples is probed using an optical technique, thus without any risk of damaging the sample. Moreover, two specific features of anodisation favour the measurement. Firstly, the electrostatic field in anodic oxide films growing under galvanostatic conditions remains constant throughout the growth process until the breakdown voltage of the oxide is reached [9]. Therefore, variations of the electrostatic stress arise from permittivity variations only. Secondly, the magnitude of the electric field developing in the film during anodising is typically on the order of 10^7 V/cm [2]. As the electrostatic stress is proportional to the square of the field, these high values provide for a large effect, readily measurable with the high curvature resolution of the proposed technique. Because the measurement is performed in-situ during anodising, it also allows for monitoring the evolution of the dielectric properties of the film during its growth. Oxide films growing anodically can undergo various morphological changes, like crystallisation, phase transitions or porosity incorporation. All these phenomena affect the density of the oxide film and hence its dielectric properties. Monitoring the evolution of the electrostatic properties of the film during anodisation can therefore help to identify the various morphological changes that occur.

2. Experimental

2.1. Sample preparation

Titanium thin films were deposited on one side of 380 μm thick (1 0 0)-oriented silicon substrates. Since the curvature measurements were performed on the backside of the anodes, double-sided polished silicon wafers were used in order to ensure good reflectivity. Prior to titanium deposition, a 400 nm thick SiO_2 layer was grown on both sides of the wafers by a wet oxidation process. This layer is intended to avoid reactions between the silicon substrate and the titanium layer upon deposition and to insulate the silicon from the electrolyte during anodisation. A 500 nm thick layer of Ti was then evaporated in a Varian e-gun device. The wafers were diced to make rectangular samples approximately 6 mm × 35 mm in size. One end of the samples was clamped in Epofix resin to ensure a cantilevered configuration.

2.2. Electrochemical setup

Anodisation of the Ti layers was carried out in an electrochemical cell made from optical glass. The cell was 10 mm × 10 mm in section and 40 mm high, thus having a volume of 4 ml. A simple two-electrode configuration was chosen and a foil of stainless steel (8 mm × 35 mm) was used as cathode. The distance between the two parallel electrodes was 5 mm. Anodic oxide films were grown under galvanostatic conditions using three different sets of experimental parameters: 1 M HNO_3 with current densities of, respectively, 1 and 3 mA/cm^2, and 1 M H_3PO_4 with a current density of 0.5 mA/cm^2. The solutions were prepared from analytical grade reagents and deionised water. A Keithley 2440 Sourcemeter was used to supply the constant current and to continuously measure the voltage drop across the cell.

2.3. In-situ curvature measurements

Curvature measurements were carried out using a multi-beam laser technique (MOS system from kSA). The curvature change of the sample was obtained from the differential spacings between multiple reflected laser beams. Fig. 1 shows a schematic illustration of the experimental setup. Details of the measurement technique and its calibration procedure for measuring in electrolytes can be found elsewhere [3]. The curvature values (κ) are converted into stress values for the oxide film (σ_{ox}) according to the well-known Stoney–Chu equation:

$$\sigma_{ox} \cdot t_{ox} = \frac{M_s \cdot t_s^2}{12} \cdot \kappa \quad (1)$$

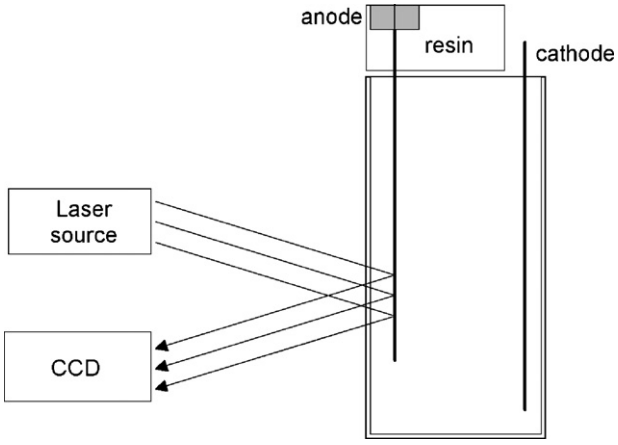

Fig. 1. Schematic illustration of the experimental setup.