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Surface patterned dielectrics by direct writing of anodic oxides using scanning droplet cell microscopy

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ABSTRACT

Scanning droplet cell microscopy was used for patterning of anodic oxide lines on the surface of Al thin films by direct writing. The structural modifications of the written oxide lines as a function of the writing speed were studied by analyzing the relative error of the line widths. Sharper lines were obtained for writing speeds faster than 1 mm min^{-1}. An increase in sharpness was observed for higher writing speeds. A theoretical model based on the Faraday law is proposed to explain the constant anodisation current measured during the writing process and yielded a charge per volume of 13.4 kC cm^{-3} for Al_2O_3. From calculated oxide film thicknesses the high field constant was found to be 24 nm V^{-1}. Electrochemical impedance spectroscopy revealed an increase of the electrical permittivity up to $\varepsilon = 12$ with the decrease of the writing speed of the oxide line. Writing of anodic oxide lines was proven to be an important step in preparing capacitors and gate dielectrics in plastic electronics.

1. Introduction

Since its development in the 90s, the capillary-based micro-electrochemical cell was continuously improved and extended e.g. by implementation of scanning capabilities [1], by the use of integrated micro-reference electrodes [2] or by the development of the contact operation mode [3] in which very high surface reproducibility was recently proven [4]. In the last period, scanning droplet cell microscopy became one of the main surface analysis tools used for mapping the electrochemical surface properties of thin film combinatorial libraries for new materials development due to its high-throughput-experimentation capabilities [5–7]. Thus, it is appropriate to define the scanning droplet cell as a new form of microscopy. Apart from imaging surface properties, the scanning droplet cell microscope (SDCM) can be used for many other types of electrochemical investigations such as grain boundary electrochemistry [8], corrosion studies with downstream analytics [9], localized photoelectrochemistry [10,11] and recently, its low required volume of electrolyte made it a perfect candidate for electrochemistry using organic electrolytes [12]. A special application of the SDCM was recently found in microelectrochemical lithography which involved localized anodic oxide growth in a point-by-point approach for surface patterning [13].

Among all valve metals, aluminium plays a key role due to the possibilities of using its protective oxide easily obtainable through anodisation [14]. The properties and behaviour of the anodic oxides can be tuned by alloying Al with other metals (e.g. Fe, Mg, W) before anodisation, leading to modified oxides [15–17]. Enhanced corrosion protection can be obtained in this manner [18]. The customization of the oxide properties extends towards the electronic applications, nanocomposite oxide films obtained by anodisation of Al alloys showing improved dielectric properties [19].

Anodised Al is an excellent dielectric for flexible electronic devices [20–24]. Direct writing of anodised oxide lines has potential for the preparation of patterned oxide structures, useful as capacitors and gate dielectrics in flexible electronic circuits. Thereby additional process steps such as optical lithography or shadow masking are avoided. Furthermore, writing potentially allows for implementation of the SDCM in roll-to-roll processing of macro-electronic items.

In the present work, the scanning capabilities of the SDCM are exploited for direct writing of continuous anodic oxide lines on flexible substrates in the sub-mm range. The lines are easily prepared under ambient laboratory conditions, avoiding additional processing such as optical lithography or shadow masking process.

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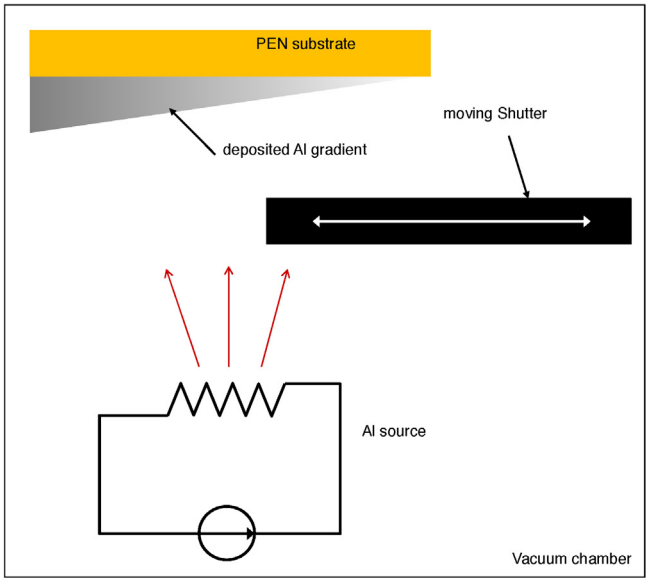

Fig. 1. Scheme of the preparation of an Al layer with a thickness gradient.

2. Experimental details

2.1. Substrate preparation

In order to investigate the possibilities of direct writing of anodic oxides, thin Al films were prepared under various conditions. A thermal evaporator with a base pressure of 10^{-4} Pa was used for the deposition of Al thin films on 50 μm thick polyethylene naphthalate (PEN) plastic substrates (Teonex Q51, obtained from Pütz GMBH + Co. Folien KG). As Al source, ultra-pure (99.9995%) Al wires (Alfa Aesar) cut in small pieces were positioned in direct contact with the surface of a W filament. The substrates were cut into rectangular stripes (10 mm × 60 mm) and were placed directly above the evaporation source at a distance of 170 mm. In order to reach the evaporation temperature of Al, a Sorenson XG 84-20 power source capable of delivering up to 1.6 kW was employed. Self-made LabView software including a PID controller was used for controlling the power delivered to the evaporation source, holding the evaporation rate at 2 nm s^{-1} during the deposition. All the Al depositions were done at room temperature and the deposition geometry allowed a maximum substrate temperature of 60 °C, reliably avoiding any thermal degradation of the PEN substrates. The evaporation rates were monitored in situ using crystal quartz balances (Testborne).

Two different series of Al thin films were evaporated. First, a uniform Al thin film with a thickness of 25 nm was evaporated, used for the oxide writing process. In a second deposition, a thickness gradient of the film was obtained in the deposited Al by using a mobile shutter placed in close vicinity to the substrate holder. The principle of the thickness wedge formation is described schematically in Fig. 1. For this special approach the sample was positioned off axis and the moving shutter ensured a prolonged exposure of only one side of the substrate to the Al vapour phase. Due to the poor step coverage dictated by the directional behaviour of Al evaporation, the shutter was actively shadowing the sample. Before evaporation, the shutter completely covered the substrate. After the desired evaporation rate was reached, the shutter was opened with a constant velocity (10 mm s^{-1}). As soon as the entire substrate was exposed to Al evaporation, the direction of the shutter movement was reversed. This resulted in an accentuated accumulation of Al at one side of the substrate, producing an Al thickness gradient. This type of sample was used for the analysis of the thickness influence on potentiostatic anodisation during the oxide writing process.

2.2. Oxide patterning process using scanning droplet cell microscope for oxide writing

Patterning of oxide on the surface of Al was achieved by employing a scanning droplet cell microscope (SDCM), where only a small electrolyte droplet comes in contact with the Al thin film. Surface oxide lines can be drawn by moving the electrolyte droplet during anodisation. This was done by using the scanning function of the SDCM. The details about the microelectrochemical cell construction were presented elsewhere [13]. For the present work two different cells were prepared. One cell with a tip diameter of 550 μm was operated in the free droplet mode [25] for the purpose of writing anodic oxide lines on the surface of Al/PEN substrate. The second cell had a tip diameter of 300 μm and was prepared for operation in the contact mode. A soft silicone sealing was formed on the rim of the capillary tip by dipping it in liquid silicone, followed by drying in N_2 flow [3]. The tip diameter of the second cell was smaller in order to allow for a complete addressing of the oxide lines written using the first cell. For both cells the counter electrode (CE) consisted of a Au band wrapped around a μ-AuHg/$Hg_2(CH_3COO)_2$/$NaCH_3COO$ reference electrode (RE) capillary. Details about the fabrication of the RE were presented elsewhere [26]. The position of the SDCM tip was controlled by a high precision *X*–*Y*–*Z* translation stage. Actuation in the *X*–*Y* plane was achieved for patterning purposes using in house developed LabView controlling software. A tilting stage ensured a planar positioning of the Al/PEN substrates. Using the vertical (*Z*) positioning, the tip was brought in contact or in close proximity to the surface of the Al/PEN substrate. A force sensor was employed to control the force applied to the Al/PEN surface during the contact mode operation [4]. In the case of the free droplet mode operation, a distance between the tip and the Al surface of approximately 20 μm was achieved corresponding to an aspect ratio of tip diameter tip distance of 1:25. For the purpose of growing a compact anodic oxide on Al, a citric acid/citrate buffer (0.265 g citric acid, 2.57 g anhydrous sodium citrate in 100 ml DI water producing a pH 6.0) was used.

A schematic drawing of the SDCM describing the anodic oxide writing process is presented in Fig. 2. An EG&G Instruments Potentiostat/Galvanostat Model 283 was used for the potentiostatic anodisation of Al thin films, which represented the working electrode (WE). Electrical contact between the potentiostat and the WE was established by pressing a W needle against the Al thin film surface. During anodisation the current was continuously monitored. In part (a) of Fig. 2 the electrical connections of the potentiostat can be seen together with the principle of oxide writing. Using the free droplet mode, a constant tip velocity combined with a constant applied anodic potential will ensure the writing of a continuous oxide line. Due to the capillary forces present between the SDCM tip and the Al surface, the electrolyte droplet will move together with the tip during the scanning/writing process, this is because it is held by capillary forces. The water evaporation due to the contact to the surrounding atmosphere was minimal because of the small proximity between the SDCM tip and the substrate surface. This fact combined with using a buffered electrolyte allowed entirely neglecting the water evaporation process over the experimentation time. A high detail photograph of the SDCM tip during the writing process of oxide lines on Al thin films is shown in Fig. 2(b). The tip of the cell is visible and no indications of gas evolution (e.g. bubble formation) could be observed. A secondary image of the cell is seen due to mirroring on the Al thin film surface. The Au counter electrode is visible inside the body of the cell giving it the golden colour. Several lines already written in previous scans are noticeable with a good contrast due to the different refractive indices of Al and Al_2O_3.