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Modulation of oxidation velocity in nanofilm processors by *in situ* electrolyte feeding

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ABSTRACT

Highly accelerated lateral oxidation of the aluminum layer in a nanofilm processor may be achieved using an electrolyte supply distributed above the aluminum layer. Localized addition of electrolyte avoids the limitation of lateral oxidation due to the length-dependent increase in hydraulic resistance of the electrolyte channel. Lateral oxidation velocities in the new devices were 25 to 30 mm per day compared to 5 to 10 mm/day in the classical nanofilm processor. We developed a model to describe the experimental results and successfully predict the lateral oxidation behavior following modifications to the experimental setup.

1. Introduction

Materials that respond to external stimuli by changing their optical properties are well known in the literature [1–3]. For instance, the transparency of liquid crystals may be modified using an external electric field [4,5], other materials exhibit temperature dependent optical properties [6–8] or a color shift by the influence of light [9], and polyaniline responds to chemical stimuli with color changes due to alteration of its doping state [10,11]. Based on this phenomena Knoll introduced the principle of self-writing based on lateral chemically-induced doping state modifications of a polyaniline layer doped with dodecyl benzene sulfonic acid [12]. This continuous change in doping state leads to a sharp color transition front that migrates laterally through the polyaniline layer in a time- and temperature-dependent manner [13,14].

In recent papers we have described a new self-writing principle based on the self-powered anodic oxidation of a nanoscale aluminum layer. The interface between the metallic aluminum and the oxidized area appears as a sharp transition from opaque to transparent. For an external observer this looks like an opening window. Due to the nanometer thickness of the aluminum layer this arrangement is referred to as a nanofilm processor. The lateral oxidation occurs in an electrochemical cell containing a graphite layer as a counter electrode [15–17].

In literature the process of anodic oxidation of aluminum is well described, where the properties of the applied electrolyte are highly significant concerning the solving behavior of the electrochemically generated aluminum oxide [18–20]. Under special conditions the formation of a regular pattern of pores in the generated aluminum oxide film is observed [21,22].

In aqueous solution aluminum in the presence of chloride ions is susceptible to oxidized by pitting corrosion processes [23–25], whereat in the pits the pH is decreased and the aluminum oxide is solved continuously[26]. This leads to a dissolving of the aluminum [26]. The nanofilm processor operates with an aqueous solution of a halide as electrolyte, so that the electrochemical processes at the interface of aluminum and the oxidized areal are comparable to pitting corrosion.

The kinetics of the pitting corrosion is correlated to the concentration of chloride ions and the pH-value of the electrolyte solution in contact to the aluminum surface, whereat a higher concentration of chloride ions is associated to an increased pitting corrosion of the aluminum [27].

In the case of nanofilm processors the electrolyte solution is provided as a thin layer of a hygroscopic halide in a polymer matrix. This layer harvest water from the ambient atmosphere and forms a concentrated halide solution in the layer, which is feed to the nanofilm processor.

The nanofilm processor technology offers a wide field of possible applications, like a labels for displaying the best-before date on food packages. The nanofilm processor also acts as a sensor for humidity [28] or temperature. With the integration of electrical switching elements [29] the nanofilm processor acts as interface for electrical devices like RFID-transducers [30].

The velocity of the moving interface between the aluminum and the oxidized area is generally 5 to 10 mm per day. In this paper

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we present a method for accelerating the lateral oxidation of the aluminum layer by modifying the electrolyte feed of the oxidation process, resulting in a more rapidly opening window in the corresponding devices. This establishes an entirely new field of application for these devices.

2. Theory

The basic nanofilm processor employing lateral anodic oxidation is depicted in Fig. 1(a). The aluminum layer is electrically connected to a counter electrode (usually graphite) with a higher standard potential than aluminum.

The electrochemical potential of the counter electrode is the result of the reduction of oxygen, whereat this proceeds in neutral or alkaline electrolytes by the peroxide pathway [31]

$$O_2 + H_2O + 2e^- \leftrightarrow HO_2^- + OH^-. \tag{1}$$

Hereby the first electron transfer step leads to the generation of hydroperoxide.

The hydroperoxide may be either transferred to hydroxide [31]

$$HO_2^- + H_2O + 2\ e^- \leftrightarrow 3\ OH^- \tag{2}$$

or decomposed to oxygen and hydroxide [31]

$$HO_2^- \leftrightarrow 0.5\ O_2 + OH^-. \tag{3}$$

The electrochemical reduction of oxygen provides a standard potential (vs. SHE) of $ECE1$ = -0.065 V(Eq. (1)) and the process shown in Eq. (2) yields a standard potential of $ECE2$ = 0.867 V (vs. SHE) [31].

Although the thermodynamics predicts a reduction of the hydroperoxide at a more positive potential than the reduction of oxygen, a large overpotential is necessary, which leads to slow down the reduction kinetics. This results in an accumulation of the hydroperoxide [31]. It is assumed that the reduction of oxygen (Eq. (1)) determines the electrochemical potential of the counter electrode, which is pH-dependent [31].

The electrolyte layer based on polyacrylic acid yields a pH of 3 [32], but during the electrochemical reduction of oxygen the pH increases due to the generation of hydroxide, which influences the electrochemical potential of the counter electrode.

At the aluminum electrode the oxidation process is separated into electrochemical oxidation of elemental aluminum given by:

$$Al \rightarrow Al^{3+} + 3e^- \tag{4}$$

and hydration of the Al^{3+} [33]:

$$Al^{3+} + H_2O \leftrightarrow AlOH^{2+} + H^+. \tag{5}$$

In an earlier work a cell potential of $ECell$ = 0.6 V was observed [16], which is caused by the electrochemical potential of the oxygen reduction at the counter electrode and the oxidation of aluminum at the anode. We assume that the electrochemical potential at the aluminum electrode is the result of pitting corrosion, which yields a pitting potential of EPC = 0.65-0.69 V [30], which differs strongly from the standard potential of the electrochemical reaction given by Eq. (4) of EAl = -1.77 V [34].

The aluminum layer is partially encapsulated to force the oxidation process in one dimension, leading to a well-defined moving interface between the unoxidized aluminum and the oxidized area, which appears optically transparent. The interface is referred to as the oxidation front or the migration front.

A laterally growing electrolyte channel remains behind the oxidation front in which charge is transferred and water is supplied for the oxidation process.

The electrolyte channel may be considered as a capillary between two parallel plates[17] in which the volumetric flow q is expressed by [35]:

$$q(t) = \frac{h^3 w}{12\eta l(t)}\Delta p, \tag{6}$$

where h is the height, w is the width, and l is the length of the electrolyte channel. The viscosity of the electrolyte medium in the channel is given by η and Δp is the pressure difference between the oxidation front and the ambient atmosphere. If the oxidation velocity is determined by the hydraulic resistance of the volume flow expressed using Eq. (6), it will decrease continuously as the length of the electrolyte channel increases.

The flow of medium in the electrolyte channel is given by [36]:

$$q(t) = \frac{dV}{dt} = hw\frac{dl}{dt} = \frac{h^3 w}{12\eta l(t)}\Delta p, \tag{7}$$

which leads to [36]:

$$\frac{dl}{dt} = \frac{h^2}{12\eta l(t)}\Delta p. \tag{8}$$

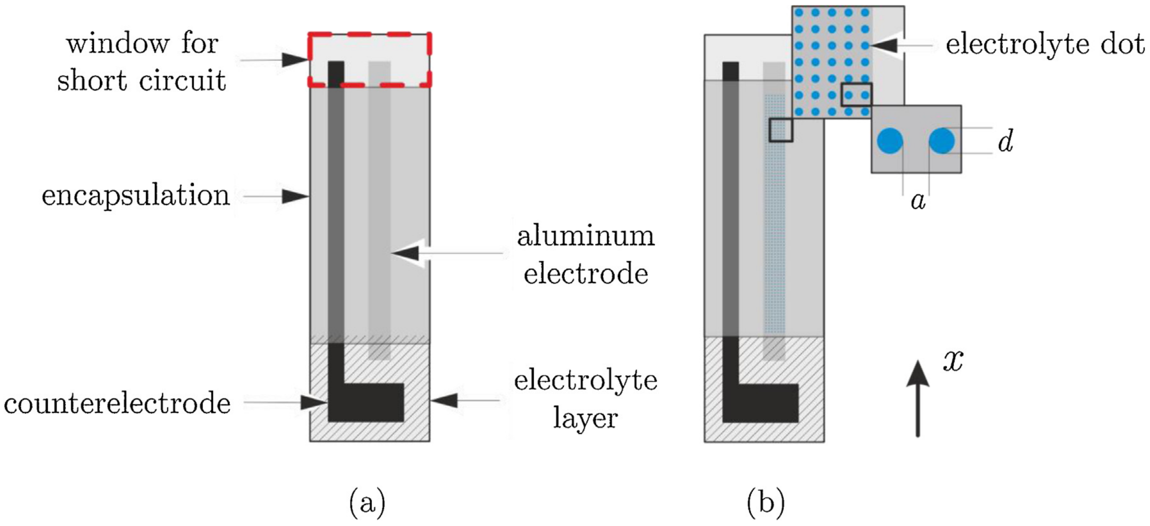

Fig. 1. Top view of nanofilm processors. (a) Classical device. (b) Device with electrolyte dot pattern on aluminum electrode. The oxidation direction is given by x.