Electrochimica Acta 224 (2017) 235–242

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Ionic transport and barrier effect of anodic oxide layer in a solid-state $Al_2O_3$ capacitor under high electric field

Manwen Yao[*,1], Jianwen Chen[1], Zhen Su, Yong Peng, Fei Li, Xi Yao

*Functional Materials Research Laboratory, School of Materials Science and Engineering, Tongji University, 4800 Cao-an Hwy., Shanghai, 201804, China*

ARTICLE INFO

*Article history:*
Received 6 August 2016
Received in revised form 4 November 2016
Accepted 7 December 2016
Available online 10 December 2016

*Keywords:*
Ionic transport
Barrier effect
Dry anodic oxidation
Aluminum
Amorphous aluminum oxide film

ABSTRACT

Dry anodic oxidation as an effective electrical self-healing method in a solid-state $Al_2O_3$ capacitor was investigated in terms of ionic transport study. Sol-gel-derived amorphous aluminum oxide (AmAO) film as dielectric and aluminum (Al) film as top electrode of the capacitor were prepared on platinized silicon substrates. When a negative voltage was applied to the Al electrode pad, the ionic transport would induce the failure of the Al electrode. Nevertheless, such failure could be inhibited by the barrier effect of an anodic aluminum oxide (AAO) layer formed at the Al/AmAO interface when positive voltage was applied to the Al electrode pad previously. The barrier effect of the AAO layer was controlled by the maximum applied positive voltage. An ionic transport model was proposed to explore the dry anodic oxidation in the solid-state $Al_2O_3$ capacitor.



## 1. Introduction

Self-healing materials are a class of smart materials which are able to heal and restore their original properties through thermal, mechanical, electrical or other means [1,2]. Self-healing polymers [3–5], ceramics, concretes [6,7], metals [8,9] and other materials have been extensively investigated for their 'self-healing of structure-mechanical function'. In addition, the 'self-healing of electric insulation function' also attracts high attentions. Aluminum electrolytic capacitor which is widely used in the electronic industry is a successful example [10]. The anodic aluminum oxide (AAO) layer newly formed at the interface between wet electrolyte and aluminum oxide dielectric layer under high electric field is able to repair small holes and other imperfections in the dielectric layer. However, the leakage problem of the wet electrolyte, especially under high temperatures, caused a lot of troubles. A solid-state electrolyte for electrical self-healing would be highly desirable [11].

Self-healing materials might be very different from their intrinsic properties, but follow the same general principle and underlying concept. For the self-healing of mechanical properties, a 'mobile phase' is an indispensable condition to close the crack, and a 'triggering factor' should be satisfied to initiate the self-healing reaction [1]. For the self-healing of the defects in dielectrics under electric field, the 'mobile-phase' means the movable cations and anions involved in the mass transfer process, and the 'triggering factor' means the local electric field around the defects. In other words, a dielectric with a self-healing function should have adequate ionic mobility, so that a new dielectric with excellent properties can be formed around the defect region through a self-healing reaction.

In our previous work [12,13], we found that the sol-gel-derived amorphous aluminum oxide (AmAO) film as an excellent dielectric medium with very high breakdown strength [14–17] can also behave as an effective solid-state electrolyte satisfied the requirement of the self-healing reaction (anodic oxidation) under high electric field at the mean time. The structures of the AmAO film and the Al film are propitious to the transport of both cations and anions involved in the anodic oxidation. The structural and absorbed water in a hydrated AmAO film is the supplier of $O^{2-}$ and/or $OH^-$ for anodic oxidation [18,19]. In this sense, it can be called as "dry anodic oxidation" and is distinguished from the anodic oxidation of liquid electrolyte. Undoubtedly, ionic transport plays a critical role in the self-healing reaction. However, the introduction of a mobile phase is a double-edged sword in solid-state capacitors, as it may introduce further problems and risks. Further works are needed to explore its potential practical applications.

In this work, failure of the Al electrode pad induced by ionic transport was observed when negative voltage was applied to the Al electrode film in the solid-state $Al_2O_3$ capacitor. This phenomenon was similar to the electromigration-induced failure of

* Corresponding author.
*E-mail addresses:* yaomw@tongji.edu.cn (M. Yao), iamjwen@126.com (J. Chen).
1 These authors contributed equally to this work and should be considered as co-first authors.

http://dx.doi.org/10.1016/j.electacta.2016.12.029
0013-4686/

aluminum electrode film in microelectronics industry [20]. It has been widely investigated to evaluate the susceptibility and reliability of the aluminum film as interconnections of the ultra-large scale integration circuits [21,22]. The failure of the Al electrode pad induced by ionic transport is also unavoidable in the solid-state $Al_2O_3$ capacitor. Nevertheless, this failure can be inhibited by the barrier effect of the AAO layer formed at the Al/AmAO interface. A delicate balance between an effective solid-state electrolyte and an excellent dielectric insulator has been achieved. Similar to the case of the anodic oxidation in liquid electrolyte, the barrier effect of the newly-formed AAO layer for ionic transport could be controlled by the maximum of the positive voltage applied. A model of the ionic transport was proposed to understand the dry anodic oxidation behavior. It is an important step toward developing practical applications of the dry anodic oxidation method in the solid-state $Al_2O_3$ capacitor.

## 2. Experimental

AmAO films were deposited onto a $10 \times 10 \times 0.5\,mm^3$ platinized silicon substrate ($Si/SiO_2/TiO_2/Pt$) using a sol-gel and spin coating technology. The preparation of AmAO films was elaborated in Ref. [23]. The thickness of the AmAO films was about 210 nm, measured by an interferometer (Filmetrics F20, San Diego, CA). Aluminum (Al) electrode pads in 1 mm diameter were deposited uniformly distributed onto the AmAO films using a ZHD-400 vacuum evaporation instrument (Technol Science, China). The distance between the centers of the electrode pads was 2 mm. The thickness of the Al films was about 100 nm measured by an anodizing method using 3% ammonium tartrate aqueous solution as electrolyte [24]. Before electrical measurement, the AmAO films were hydrated at room temperature under relative humidity of 50% for 60 min in a GP/TH-50 humidity chamber (Guangpin, China). Leakage current–voltage (I–V) characteristic was measured by using a Keithley 2400 source meter (Keithley Instruments Inc., USA). Surface morphology was examined by an atomic force microscope (AFM; Dimension ISON SPM, Bruker, USA), a BX51 optical microscope (Olympus) and a field emission scanning electron microscope (FESEM; FEI Quanta 200 FEG).

## 3. Result and discussion

Ionic transport plays a critical role in the electrical self-healing process of the solid-state $Al_2O_3$ capacitors. However, the introducing of a mobile phase (ionic transport) might result further problems and risks in the performance of the capacitors, such as the electromigration-induced failure of Al electrode film observed in microelectronics industry [25,26]. Ionic transport would induce such failure of the microelectronic devices when negative voltage is applied.

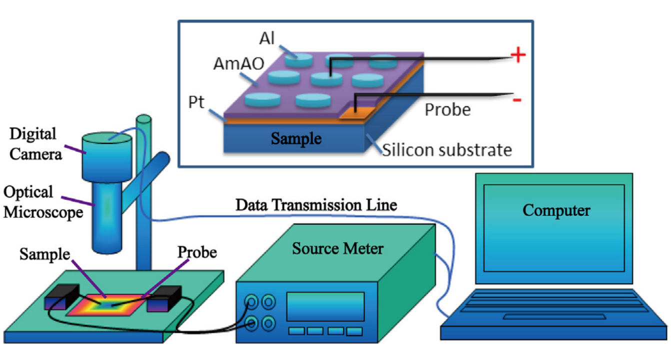


**Fig. 1.** Schematic diagram of the test equipment.

Fig. 1 is the schematic diagram of the test equipment. I–V of the AmAO capacitors with Al electrode pad was characterized when a negative ramping voltage was applied at a rate of 0.2 V/step and an interval of 0.5 s. To understand how the surface morphology of the Al electrode pad would change under the applied negative voltages, the samples were monitored and recorded under an optical microscope in real-time during the entire testament. Since the intensity of the reflected and scattered light from a surface revealed information about the surface roughness [27,28], we recorded the microscope images under dark-field illumination at different time/voltage nodes.

As shown in Fig. 2, the Al electrode pad gradually turned into white as the negative ramping voltage increased from −10 to −30 V. Then the current suddenly dropped from micro- to nano-amperes at the voltage of −45 V. The bluish white color under dark-field illumination suggests that the surface roughness of the Al electrode pad increased during the test. The sudden reduction of the leakage current of the AmAO sample signifies the occurrence of the pad failure.

Fig. 3 is the I–V characteristics of the AmAO sample under cyclic voltammetric examination. A triangle cyclic voltage with maximum voltage of ±40 V was applied to the sample. For the positive half of the first cycle, in the rising branch of the applied voltage from 0 to 40 V, the leakage current sharply increased up to a maximum of 3.1 μA at 9 V, and then decreased down gradually to 2 μA as the voltage increased from 9 to 40 V. An AAO layer started to grow at the metal/film interface when the positive voltage was applied to the Al electrode pad. The thickness of the AAO layer increased with the increasing of the positive voltage [13]. The formation of the growing AAO layer increased the total thickness of the alumina layer and passivated the Al electrode as well, hence, the leakage current reduced as the voltage increased from 9 to 40 V. In the descending branch of the applied positive voltage, as a result of the newly-formed AAO film, the leakage current is much lower than that of the rising branch. For the negative half of the first cycle, the leakage currents of the rising and descending branch along the negative direction are quite close to each other and exhibit typical nonlinear characteristics of conductivity. It should be noted, that the absolute value of the leakage current under higher negative applied voltage is always a little higher than that of the corresponding positive voltage. However, the leakage current of the sample after the first positive voltage cycling, −56 nA at −20 V for example from Fig. 3, is substantially lower than that of the virgin sample under same negative applied voltage, −2 μA at −20 V as shown in Fig. 2. As to the second and third cycles, the leakage currents decreased further slightly as shown in Fig. 3. In considering the fact that more and better AAO films can be formed during the repeating application of positive voltage, the reduction of leakage currents in the second and third cycles can be well understood.

The failure of the Al electrode film under negative voltages can be avoided after the application of the positive voltage previously. There is almost no change in surface morphology of the Al pad electrode after the cyclic voltammetric treatment except for a bright stripe along the edge of the electrode (Fig. 3). The bright stripe is attributed to the priority anodic oxidation of the Al electrode pad owing to the edge effect [13]. It is suggested that the surface roughness of the Al electrode pad has almost no change after 3-cyclic voltammetric measurements.

Fig. 4 is the AFM images showing the surface morphology of the Al electrode pad before and after the voltammetric characteristic measurement (Fig. 4a–4c). The root mean square average of the height deviations in these AFM images is 2.47, 16.5 and 2.52 nm corresponding to the initial state (Fig. 4a), after the application of negative voltage (4b) and after 3-cycles of voltammetric measurement (4c). The surface roughness of the Al electrode pad is