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

Manwen Yao^{*,†}, Jianwen Chen[†], Zhen Su, Yong Peng, Fei Li and Xi Yao

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.

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

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].

1 Self-healing materials might be very different from their intrinsic properties, but follow the same general
2 principle and underlying concept. For the self-healing of mechanical properties, a ‘mobile phase’ is an
3 indispensable condition to close the crack, and a ‘triggering factor’ should be satisfied to initiate the self-healing
4 reaction [1]. For the self-healing of the defects in dielectrics under electric field, the ‘mobile-phase’ means the
5 movable cations and anions involved in the mass transfer process, and the ‘triggering factor’ means the local
6 electric field around the defects. In other words, a dielectric with a self-healing function should have adequate
7 ionic mobility, so that a new dielectric with excellent properties can be formed around the defect region through
8 a self-healing reaction.
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10 In our previous work [12, 13], we found that the sol-gel-derived amorphous aluminum oxide (AmAO) film
11 as an excellent dielectric medium with very high breakdown strength [14-17] can also behave as an effective
12 solid-state electrolyte satisfied the requirement of the self-healing reaction (anodic oxidation) under high electric
13 field at the mean time. The structures of the AmAO film and the Al film are propitious to the transport of both
14 cations and anions involved in the anodic oxidation. The structural and absorbed water in a hydrated AmAO
15 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
16 oxidation” and is distinguished from the anodic oxidation of liquid electrolyte. Undoubtedly, ionic transport
17 plays a critical role in the self-healing reaction. However, the introduction of a mobile phase is a double-edged
18 sword in solid-state capacitors, as it may introduce further problems and risks. Further works are needed to
19 explore its potential practical applications.
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21 In this work, failure of the Al electrode pad induced by ionic transport was observed when negative voltage
22 was applied to the Al electrode film in the solid-state Al_2O_3 capacitor. This phenomenon was similar to the
23 electromigration-induced failure of aluminum electrode film in microelectronics industry [20]. It has been
24 widely investigated to evaluate the susceptibility and reliability of the aluminum film as interconnections of the
25 ultra-large scale integration circuits [21, 22]. The failure of the Al electrode pad induced by ionic transport is
26 also unavoidable in the solid-state Al_2O_3 capacitor. Nevertheless, this failure can be inhibited by the barrier
27 effect of the AAO layer formed at the Al/AmAO interface. A delicate balance between an effective solid-state
28 electrolyte and an excellent dielectric insulator has been achieved. Similar to the case of the anodic oxidation in
29 liquid electrolyte, the barrier effect of the newly-formed AAO layer for ionic transport could be controlled by
30 the maximum of the positive voltage applied. A model of the ionic transport was proposed to understand the dry
31 anodic oxidation behavior. It is an important step toward developing practical applications of the dry anodic
32 oxidation method in the solid-state Al_2O_3 capacitor.
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2 Experimental

AmAO films were deposited onto a $10 \times 10 \times 0.5 \text{ mm}^3$ platinized silicon substrate ($\text{Si}/\text{SiO}_2/\text{TiO}_2/\text{Pt}$) 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.

Figure 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 test. 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 Figure 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.

Figure 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 μ A at 9 V, and then decreased down gradually to 2 μ A 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 -20V for example from Figure 3, is substantially lower than that of the virgin sample under same negative applied voltage, -2 μ A at -20 V as shown in Figure 2. As to the second and third cycles, the leakage currents decreased further slightly as shown in Figure 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 (Figure 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.

Figure 4 is the AFM images showing the surface morphology of the Al electrode pad before and after the voltammetric characteristic measurement (Figure 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 (Figure 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 apparently affected by the application of the negative voltage, but has

almost no change, after 3 cyclic voltammetric measurements.

Figure 5 is the FESEM images of the surface morphology of the Al electrode pad before and after electrical measurements. Figure 5(a) is the initial state of the aluminum electrode before electrical measurement. The initial Al electrode pad was composed of nanoparticles of about 100 nm. However, numerous voids and hillocks as shown in Figure 5(b) appeared at the surface of Al electrode pad after the application of negative voltage, which signifies the occurrence of mass transport within the electrode under negative voltages. The surface morphology of the Al electrode pad after 3-cyclic voltammetric measurements, Figure 5(c), has almost no change or even getting a little denser in comparison with its initial state. The failure induced by ionic transport under negative voltages as exhibited in Figure 5(b) can be effectively inhibited by the previously applied positive voltage in the cyclic measurement. The cross-sectional FESEM image, Figure 5d, after the 3 cyclic voltammetric measurements is a strong evidence on the formation of the anodic aluminum oxide (AAO) layer at the Al/AmAO interface. It is suggested that the newly-formed AAO layer inhibited the formation of voids and hillocks in the Al electrode film.

In general, the roughness variation of the Al electrode under applied negative voltages could be mainly induced by two different ways, cathodic corrosion and mass transport. Cathodic corrosion of Al would be one of the most probable mechanisms for Al pad failure under negative voltage, especially in the aqueous solution media, since the applied negative potentials of the Al pad is very high [29-31]. Cathodic corrosion is anodic corrosion induced by the pH increase at an Al electrode under cathodic polarization. The electrochemical reaction can be represented as follow:

However, in this work, although the hydrated AmAO film can be regarded as a kind of solid electrolyte, it is still a dielectric material in nature. The movable OH^- anions are much less than that of the aqueous solution electrolyte. In our previous work [13], we have found that the water absorbed in the hydrated AmAO film with a 210 nm thickness is so little that is insufficient to transform a 65 nm thick Al electrode film completely from metal state into oxide state. In a water-starved environment, aluminum cations Al^{3+} could be migrated toward and arrived at the Al pad. In fact, similar phenomenon which is called as ‘electromigration-induced failure’ has been reported in microelectronics industry [26, 32, 33]. Arthur J. Learn [32] has studied the electromigration-induced failure in anodized aluminum, where the structure of the sample is similar to the one that used in this work.

As a reasonable explanation to the failure as shown in Figure 2, when a negative voltage was applied to the Al electrode pad, the anions (O^{2-}/OH^-) formed in the hydrated AmAO film would migrate toward the positive Pt electrode and the vacancies left from the migrated O^{2-}/OH^- condensed to form voids. In the meantime, the cations (Al^{3+} and H^+) would migrate toward the negative Al electrode pad. The Al^{3+} cations traveled toward the negative Al electrode pad, caught electrons, reduced back to Al^0 and piled up to form hillocks, while the H^+ turned into H^0 and released from the film leaving opening channels at the surface.

When a cyclic voltammetric measurement was applied to the sample in the manner exhibited in Figure 3, the positive voltage applied on the Al electrode pad during the initial first cycle promoted the growth of a dense AAO layer at the AmAO/Al interface via electrochemistry reaction. It is suggested that the newly-formed AAO layer inhibited the formation of voids and hillocks in the Al electrode film. The positive voltage during the cycling measurement also helped to drive back the mass transport process of the Al electrode taking place under negative voltage in the following cycling. Both actions inhibited the change of surface roughness of the Al electrode. It will be confirmed and discussed next further in detail.

Upon the application of the positive voltage, the anions O^{2-}/OH^- formed in the hydrated AmAO film would oxidize the aluminium at the Al/AmAO interface, thereby transforming Al atoms into aluminium oxide and/or hydroxide, forming an anodic oxide layer at the Al/AmAO interface. This process is similar to the anodic oxidation in liquid electrolyte [34-37]. The structural and absorbed water of the hydrated AmAO film, which acts as an effective solid state electrolyte, is supposed to be the supplier of O^{2-} and/or OH^- for anodic oxidation [18, 19]. The reactions at the anode and cathode might be described as follows:

Anode:

Cathode:

A barrier oxide layer was formed at the Al/AmAO interface after the application of positive voltage. According to the theory of barrier-type anodic oxide film growth [24, 38], the thickness of the newly-formed oxide layer depends on the positive voltage applied to the Al electrode pad. It has been found that the thickness of the newly-formed aluminum oxide film increased linearly with the positive voltage at a slope of 0.456 ± 0.001 nm/V [13].

According to the theory of anodic oxidation growth, there are two basic kinetic oxidation modes: constant current control mode and constant voltage control mode. In the current control mode, the current is kept constant, the voltage and thickness of the newly-formed oxide film increase linearly with time. In the voltage control mode, the voltage is kept constant, the current and growth rate of the oxide film decrease rapidly with time. In this work, both modes were used to investigate the anodic oxidation characteristics of the Al/AmAO configuration.

As shown in Figure 6, starting to anodize the Al pads of the Al/AmAO/Pt configuration in a constant current mode, set the constant current to 1 μA (1.27 A/m^2), the voltage across the test sample increased with the increasing of time approximately in a linear way. Anodizing the test aluminum pads one by one until an upper limit voltage of 10, 20, 30, 40 and 50 V reached then turned into the constant voltage mode for a total time of 500 s each. The initial voltages of these five test sample are 1.30, 12.30, 24.06, 35.27 and 46.29 V respectively. In the voltage control mode, the current decreased with time exponentially following Eq. 8, where the root mean square error (RMSE) of the fitting curves is lower than 2.5%. It suggests that the anodic oxidation after the application of the electric field of the Al electrode pad significantly increased the DC resistance of the test sample.

$$I(t) = I_0 + I_l \cdot \exp\left(-\frac{t}{\tau}\right) \quad (8)$$

Similar to the barrier-type anodization in a liquid electrolyte, the ionic charge transport obeys the Cabrera-Mott theory. The field strength is determined by the voltage drop across the oxide film divided by its thickness. The ionic current density (J_+) and electric field strength (E) are related exponentially, which is controlled by the Cabrera-Mott theory (or metal-oxide interface control) [36] as follows:

$$J_+ = nvq \exp\left(-\frac{W - qaE}{kT}\right) \quad (9)$$

where n is the density of cation and anion at the Al/AAO interface; ν is the vibrational frequency of surface atoms; q is the charge of mobile ions; W is the height of the energy barrier over which the ions must pass before entering the oxide bulk; k is the Boltzmann's constant and T is the absolute temperature.

Therefore, the ionic conduction is negligible below the formation voltage of the AAO layer. In other words, if a positive voltage of +40 V had applied to the test sample to form AAO layer, the ionic conduction under negative voltage below absolute value of -40 V would be almost negligible. The cations (Al^{3+} and H^+) formed in the hydrated AmAO film migrated to the Al electrode pad but were blocked at the AmAO/AAO interface. Meanwhile, the anions (O^{2-} and OH^-) that left in the Al electrode film after the application of positive voltage were also blocked at the Al/AAO interface. As a result, the newly-formed AAO layer prevented the formation of

voids and hillocks in the Al electrode film.

In addition, the ionic current of the newly-formed AAO layer would increase significantly when the negative voltage rose up to the AAO formation voltage. In other words, the barrier effect of the AAO layer was controlled by the maximum of the positive voltage applied. After the positive upper limit voltages of 5.0, 10.0, 15.0 and 20.0 V were applied to the Al electrode pad, current peaks appeared at -6.4, -10.8, -16.0 and -20.6 V, respectively (Figure 7). The absolute values of the peak voltage were slightly higher than the maximum positive voltage.

Figure 8 is a model of ionic transport mechanism proposed to reveal this phenomenon. Compared with the initial state of the solid-state Al_2O_3 capacitor (Figure 8c), an AAO layer was formed at the Al/AmAO interface after the positive voltage was applied to the Al electrode pad (Figure 8d). As discussed above, below the voltage of -10 V, the cations (Al^{3+} and H^+) formed in the hydrated AmAO film migrated to and were blocked by the newly-formed AAO film at the AmAO/AAO interface, while the anions (O^{2-} and OH^-) leaving the Al electrode film were blocked at the Al/AAO interface (Figure 8e).

As the negative voltage increased to -10 V, the leakage currents of the newly-formed AAO layer increased rapidly with time. At this point, the cations (Al^{3+} and H^+) accumulated at the AmAO/AAO interface and the anions (O^{2-} and OH^-) gathered at the Al/AAO interface could pass through the AAO film (Figure 8f). Then the cations, anions and electrons migrated toward each other and recombined, which resulted in a sudden increase of the leakage current passing through the new AAO layer. The ionic recombination consumed numerous ionic charge carriers (Figure 8f). Then the leakage current suddenly decreased when the absolute value of the negative voltage was close to the maximum positive voltage applied previously. It suggests that the barrier effect of the new oxide layer can be controlled by the positive voltage applied before.

Figure 9 is the I-V characteristics during the cyclic voltammetry at 25, 35, 45 and 55 °C. Clearly, the current density increased with temperature rising. The negative current density increased more significantly than the positive current density, which can be attributed to the barrier effect of the newly-formed AAO layer and the consumption of charge carriers (ions) during anodic oxidation. More importantly, the peaks on the I-V curves appeared near -10 V were temperature dependent.

4 Conclusions

Ionic transport would induce the failure of the Al electrode pad when negative voltage was applied to the Al electrode in the solid-state Al_2O_3 capacitor. This failure can be inhibited by the barrier effect of the anodic oxide layer formed at the Al/AmAO interface. A barrier-type AAO layer was formed at the Al/AmAO interface

when positive voltage was applied to the Al electrode pad. The barrier effect for the ionic transportation of the newly-formed AAO layer was controlled by the maximum positive voltage applied previously. A delicate balance between an effective solid-state electrolyte and an excellent dielectric insulator has been achieved.

Acknowledgment

This work is supported by the Ministry of Science and Technology of China through 973-project (Grant Number 2015CB654601), National Science Foundation of China (Grant Number 51272177) and International Science & Technology Cooperation Program of China (Grant Number 2013DFR50470).

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Figure captions

Figure 1 Schematic diagram of the test equipment.

Figure 2 I-V characteristics and real-time optical microscopy images in dark-field illumination for the Al electrode pad during the negative ramping voltage.

Figure 3 I-V characteristics and real-time optical microscopy images under dark-field illumination of the Al electrode pad before and after positive and negative cyclic voltage scanning : (a) initial state, (b) after the first cycle and (c) after the third cycle.

Figure 4 AFM images showing the surface morphology of the Al electrode pad before and after electrical measurement: (a) Initial state before measurement; (b) After the application of negative ramping voltage corresponding to Figure 2d; (c) After 3 cyclic voltammetric measurements corresponding to Figure 3c.

Figure 5 FESEM images showing surface morphology of the Al electrode pad before and after electrical measurements: (a) Initial state before measurement; (b) After the application of negative ramping voltage; (c) After 3 cyclic voltammetric measurement; (d) Cross-sectional image after 3 cyclic voltammetric measurements.

Figure 6 Voltage (a) and Current (b) vs. Time of the hydrated AmAO film with Al electrode pad in constant-voltage and constant-current control modes.

Figure 7 I-V characteristics during the cyclic voltammetry with different maximum values of positive voltage. The time variation of the voltage of (a), (b), (c) and (d) are given in (f).

Figure 8 Model of ionic avalanche and barrier effect of the AAO layer during the cyclic voltammetry.

Figure 9 I-V characteristics during the cyclic voltammetry with the maximum positive voltage of 10 V at 25, 35, 45 and 55 °C.

Figure 1

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Figure 3

Figure 4

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Figure 8

Figure 9