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Self-healing effect based on electrolyte/dielectric co-existence characteristic of sol–gel-derived aluminum oxide thin film

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Dielectric capacitors are receiving increasing attention due to the high-power density and fast charge–discharge speed. However, defects are inevitably induced during the preparation process and then weaken the breakdown strength, thereby limiting their energy density. The phenomenon gives rise to self-healing technology. The discovery of sol–gel-derived aluminum oxide with electrolysis and dielectric dual-characteristic provides a novel, simple and cost-effective self-healing method to heal defects and enhance energy density. In this paper, we systematically reviewed the current self-healing technologies and the important progress of electrolysis and dielectric co-existence dielectrics. Finally, we outlook the electrolysis and dielectric co-existence dielectrics and potential challenge.

Keywords: Electrolyte/dielectric co-existence; self-healing effect; sol–gel method; aluminum oxide.

1. Introduction

Dielectric capacitors store electrical energy *via* dielectric polarization. Dielectric capacitors exhibit high power density and ultrafast charge–discharge speed, and have been used in pulsed power electronics.[1–3] However, dielectric capacitors still suffer from a low energy density, which limits their further applications. Generally, the energy density of a dielectric capacitor (U_e) is determined by breakdown strength (E) and dielectric polarization (P) according to formula (1)[4]:

$$U_e = \int_{P_r}^{P_{\max}} \mathrm{EdP}, \tag{1}$$

where E is the breakdown strength, P is the polarization parameter, $P_{\max}$ and P_r are the maximum polarization and remnant polarization, respectively. Therefore, the way of enhancing breakdown strength and improving polarization performance (large $P_{\max}$ and small P_r) is usually employed to achieve a high energy density. In the past decades, great progress and breakthrough have been made in improving energy densities of dielectrics.[5] For example, energy densities of ceramic blocks, dielectric film and organic-based dielectrics have exceeded 10, 100 and 35 J cm^{-3}, respectively. However, the way of improving breakdown strength and dielectric constant focuses on the selection and modification of dielectrics,[6–8] such as doping nanomaterials into dielectrics,[9,10] preparing multi-layer dielectrics[11,12] and so on. No matter what kinds of technologies, defects, like interfacial defects between electrode and dielectrics and structural defects of dielectrics are inevitably induced, the presence of such defects gives rise to an inhomogeneous local electric field, thereby initiating the phenomenon of the breakdown. As the volume and plate area of the capacitor increase, the internal structural defects increase, thereby exacerbating the issue at hand. Furthermore, the breakdown events could lead to local heating and rapid vaporization of the material to produce larger defects.[13]

The defects are inevitable. Therefore, healing/repairing these defects is necessary for enhancing the energy density and promoting the development of dielectric capacitors. This review concluded the common self-healing technologies and the novel technique based on the electrolyte/dielectric co-existing sol–gel-derived aluminum oxide thin film, applied in the dielectric capacitors. The new type of dielectric material shows electrolyte properties which could anodize valve metal to produce new dielectrics. The new dielectrics could repair the interfacial defects between dielectrics and electrode.

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Moreover, the initial dielectric exhibits an inherent self-repairing phenomenon within its structure. This is a novel technique for the self-healing dielectric capacitors. We hope this paper provides researchers with a comprehensive understanding of this novel dual-function dielectric material and its associated innovative self-healing approach, thereby offering a new avenue for the development of high-energy-density dielectric capacitors.

2. Self-Healing Model

The self-healing model can be categorized into three types: (a) Dielectric breakdown events result in vaporization of both the dielectric materials and surrounding electrode. The formed damage site becomes electrically isolated from the applied electric field, achieving a healing effect. However, with continued breakdown events, the performance progressively deteriorates (as shown in Fig. 1(a)). (b) Defects are generated and subsequently healed and/or infilled with chemical and nonchemical approaches. The method can maintain device functionality without any area/volume loss (Fig. 1(b)). (c) Microcapsules containing healing materials are pre-filled within the dielectrics. The microcapsules release healing agents to realize self-healing as breakdown trees rupture the microcapsules (Fig. 1(c)).

There are three types of commercial capacitor products utilizing self-healing technology: (a) Metallized film capacitors,[14] (b) aluminum electrolytic capacitors and (c) tantalum solid-state capacitors.[15] Metallized film capacitors do not actually repair defects, but rather insulate them through the thermal evaporation of the metal electrode, as described in the first self-healing model.[16,17] However, this repair mechanism often leads to irreversible changes in the internal structure of the capacitor, resulting in capacity loss. Typically, the capacitance of metallized film capacitors ranges from 1000 pF to 4.7 μF. Aluminum electrolytic capacitors consist of aluminum metal foils as the anode, a valve metal oxide film (Al_2O_3) formed on the surface of the anode metal foil as the dielectric and a working electrolyte absorbed by a porous electrolytic paper serving as the cathode. Utilizing the equation $C=\varepsilon r^*A/d$, the capacitor achieves a large capacitance value (C) by significantly increasing the electrode area (A) through winding. Moreover, aluminum electrolytic capacitors use the anodic oxidation of aluminum foil in liquid electrolyte to realize the self-healing of defect. Due to the increased electrode area (A) and the self-repairing effect, the capacitance value of the capacitor can reach up to 1000000 μF. But the existence of liquid electrolyte will probably lead to electrolyte leakage, decomposition and evaporation, resulting in capacitor explosion and other problems. Tantalum electrolytic capacitor is made from tantalum metal, serving as the anode, with a layer of oxide acting as the dielectric, and surrounded by a conductive cathode. Tantalum solid capacitor[15,18] can form a new oxide layer near the dielectric film under an electric field by introducing solid electrolyte MnO_2, so as to achieve the purpose of defect self-healing. The self-healing effect maintains the capacitor system always in stable state even under a high electric field. Tantalum solid capacitor uses solid MnO_2 as electrolyte, which is safer and more stable than liquid electrolytic capacitor. Furthermore, tantalum oxide exhibits a relatively higher dielectric constant, particularly significantly higher than that of aluminum oxide (Al_2O_3). Consequently,

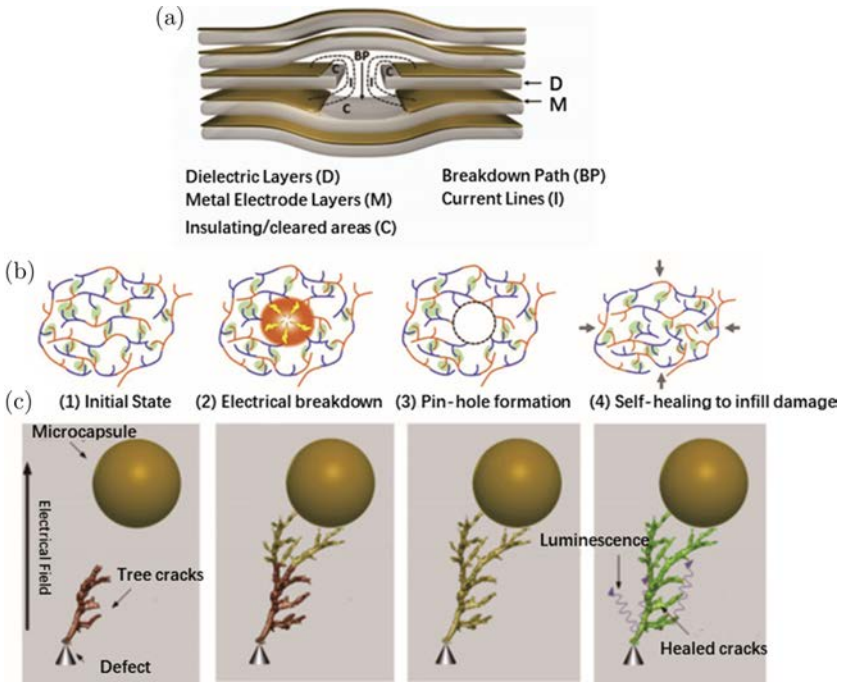

Fig. 1. Demonstration of three types self-healing model.[13]

Table 1. The three self-healing capacitors' characteristics.

Self-healing pacitors	Mobile phase	Stimulation conditions	Self-healing response	Capacitance range	Remark
Metallized film capacitors	/	Large local electric field near defect or damage	/	1000 pF–4.7 μF	Defects are insulated by thermal evaporation of the film metal electrode.
Aluminum electrolytic capacitors	OH^- and O^{2-}	Large local electric field near defect or damage	Anodizing reaction of aluminum electrodes	0.1– 1000000 μF	Reaction-generated Al_2O_3 has the characteristics of high electrical resistance and low-leakage conductance to repair defects and suppress leakage current near the local electric field.
Tantalum solid capacitors	O_2 decomposed from MnO_2	Large local electric field near defect or damage	Oxidation of tantalum metal	0.1–3300 μF	Reaction-generated Ta_2O_5 has the characteristics of high electrical resistance and low leakage conductivity, which repairs defects and suppresses the leakage current of the local electric field.

tantalum electrolytic capacitors with the same volume and similar structure have a larger capacitance compared to aluminum electrolytic capacitors. Currently, tantalum capacitors commonly available in the market have capacitance values ranging from 0.1 μF to 3300 μF. However, their high price, low capacitance and large volume of MnO_2 electrolyte limit the improvement of the capacitor. The three capacitors' characteristics are summarized in Table 1.

3. Sol–Gel-Derived Aluminum Oxide Thin Film

As mentioned above, the electrolysis properties could realize the self-healing effect. Aluminum could be anodized to form aluminum oxide. Moreover, aluminum oxide possesses outstanding mechanical, optical, chemical, thermal and electrical properties[19] and finds extensive applications in catalyst carriers, ultra-filtration and separation films and other fields.[20,21] Meanwhile, aluminum oxide, as a kind of dielectric, shows a high breakdown strength, a low leakage current and a low dielectric loss, making it a promising candidate for high energy density capacitors.[22,23] Therefore, aluminum and aluminum oxide exhibit a tremendous potential for the development of traditional capacitors.

Aluminum oxide thin film can be fabricated using various techniques, including chemical vapor deposition,[24,25] electron beam evaporation,[26] anodization,[27] magnetron sputtering[28] and sol–gel method.[29,30] Among these methods, the sol–gel method offers distinct advantages in terms of its simplicity, cost-effectiveness and the ability to precisely control the chemical compositions of the target material.[31] Moreover, the sol–gel-derived aluminum oxide dielectric material has been found to possess electrolysis properties. The innovative dielectric allows the anodization of valve metal, such as Al, Ti, Cu and so on, resulting in the formation of oxides at the interface between the electrode and the dielectric, as shown in Fig. 2. Simultaneously, the sol–gel-derived aluminum oxide

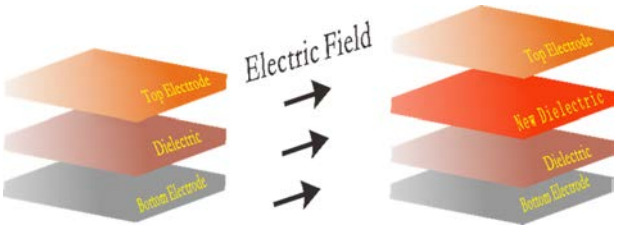

Fig. 2. Schematic of production of newly formed oxides (dielectrics) under a high electric field.

could heal itself under high electric fields. These oxides display either a high breakdown strength or a high dielectric constant and the self-healed-aluminum-oxide demonstrates an elevated breakdown strength, thereby enhancing the energy density of the device. The method capitalizes on the unique characteristic of electrolysis and dielectric properties inherent in the sol–gel-derived alumina thin film.

3.1. *Aluminum oxide–H_2O system*

The electrolysis of sol–gel-derived aluminum oxide is attributed to the presence of water molecules and/or hydroxyl groups. Water molecules play a crucial role in the structure and reactivity of aluminum oxide. According to the presence of water molecular, aluminum oxide exists in many metastable polymorphs, which is also known as transition aluminum oxides, besides the thermodynamically stable α-Al_2O_3, as indicated in Table 2.[32] These transition aluminum oxides are generated through the thermal treatment of aluminum oxide precursors at temperature below 800°C and exhibit a high specific surface area.[33] Theoretically, Al atom and O atom are ideally alternatively bonded. However, some defects are bound to exist, which will result in some break bonds. Specifically, oxygen-terminated broken bonds can combine with water molecules or hydroxyl groups, resulting in the

Table 2. Various crystallines of aluminum oxide and their structural parameters.[32]

Crystalline		α	κ	θ	δ	χ	η	γ	ρ
Compounds		← Water content reduction							
Crystal system		Trigonal	Orthorhombic	Mono-clinic	Tetragonal/ orthorhombic	Hexagonal	Cubic	Cubic	Closed-to-amorphous
Space groups		R-$\bar{3}$c	$Pna2_1$	C_{2h}^3	P212121	P6/mm or P63/mcm	O_h^7	Fd$\bar{3}$m	/
Density/g·cm^{-3}		3.98	3.1–3.3	3.4–3.9	3.2	3.0	2.5–3.6	3.2	3.96
Lattice parameters × 10^{-10} m	a	4.758	4.69	11.24	7.94	5.56	7.92	7.95	/
	b	4.758	8.18	5.72	7.94	5.56	7.92	7.95	/
	c	12.991	8.87	11.74	23.5	13.44	7.92	7.79	/

formation of different aluminum oxides species. Depending on the nature of the interaction between O atoms and water molecules/hydroxyl groups, the water molecules can be categorized into three categories: (a) Physical adsorption water molecules, (b) chemical adsorption water molecules and (c) free water molecules, as shown in Fig. 3(a). The chemical adsorption of water molecules involves the formation of chemical bonds with O atoms. The physical adsorption water molecule is bonded with O atoms in the form of hydroxyl bonds.

In addition to the water molecules inside the aluminum oxide, a significant amount of lots of water molecules are generally adsorbed onto the surface of the aluminum oxide.[34] Eng *et al*. reported that an oxygen-terminated surface was coupled with a contact water layer.[35] Similarly, water molecules can also be adsorbed onto Al-terminated and OH-terminated surfaces, as depicted in Fig. 3(b). At distances greater than approximately 10 Å from the substrate, water molecules exhibit bulk-like behavior. The interaction between aluminum oxide and water (Aluminum oxide-H_2O system) is complex and the presence of water imparts electrolysis properties to the aluminum oxide material.

The presence of water content in the aluminum oxide can have a significant impact on its dielectric response. Water molecules can interact with the oxide material in different ways, leading to distinct dielectric behaviors. Water condenses on the surface and forms a conducting path around the particles, which appears as a high dielectric constant and is associated with ionic conduction, thereby increasing the leakage current. Physical adsorption water molecules that are trapped in capillaries or voids within the aluminum oxide structure, do not contribute significantly to the dielectric properties of the material and are considered to be relatively immobile. Their relaxation typically occurs at higher frequencies, around 12 GHz and their presence is associated with ionic conduction and also increases leakage current. Chemical adsorption water molecules can react with the aluminum oxide to form hydroxide species. These hydroxides exhibit a distinct dielectric relaxation centered at lower frequencies, around 10 kHz. The relaxation is typically attributed to the rotation of OH groups within the hydroxide.

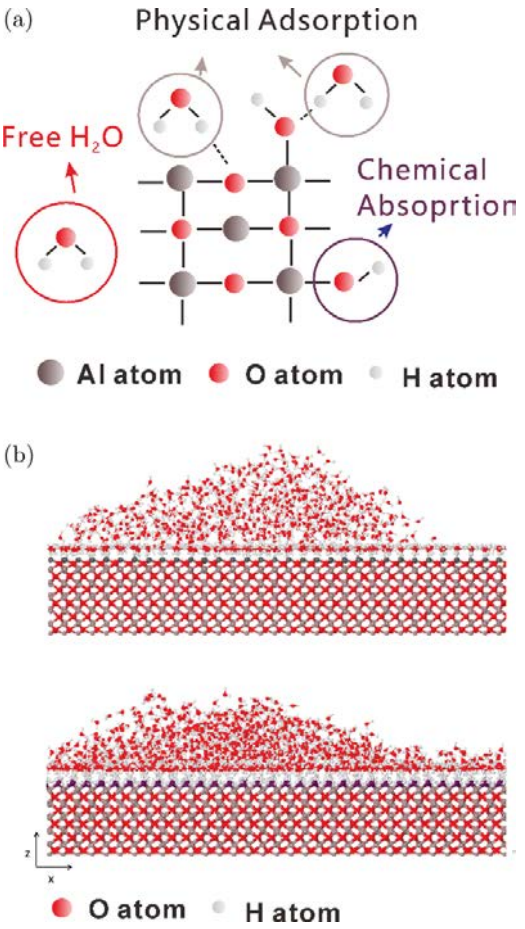

Fig. 3. (a) Various types of water molecules embedded in aluminum oxide; (b) Side views of the Al-terminated (top) and OH-terminated (bottom) aluminum oxide surfaces with 2000 water molecules.[36]

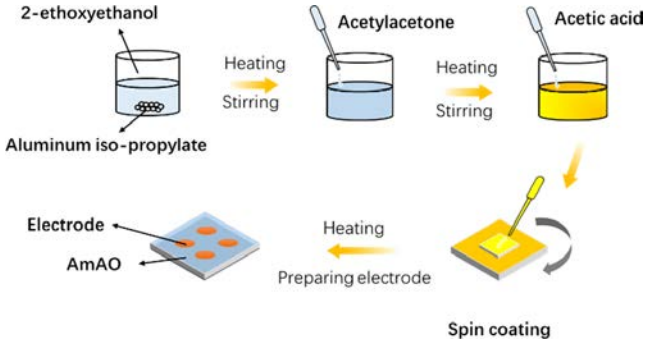

Fig. 4. The schematic of the preparation of aluminum oxide thin film.[42]

3.2. *The preparation of aluminum oxide thin film by sol–gel method*

To date, the sol–gel-derived aluminum oxide was only found to exhibit both electrolysis and dielectric properties. The sol–gel method offers a convenient approach for coating various substrates, including glass, plastics, metals and ceramics. Furthermore, the sol–gel technique provides excellent homogeneity, low annealing temperature and high purity of the resulting film.[37,38] The preparation of aluminum oxide thin film via the sol–gel method can be categorized into two types based on the aluminum precursors: Inorganics-based sol–gel method[39,40] and organics-based sol–gel method.[41]

In this paper, the organic-based sol–gel method was concretely discussed. The preparation route is shown in Fig. 4. The aluminum iso-propylate was chosen as aluminum precursor and 2-ethoxyethanol as solvent. Aluminum iso-propylate of 4.048 g was dissolved in 50 mL 2-ethoxyethanol at 70°C for 30 min. 2.002 g acetylacetone as a chelating agent was added to the above solution and then stirred at 70°C for 30 min. Subsequently, 10 mL acetic acid was added to the solution to obtain aluminum sol. The sol was spin-coated onto the substrate (Pt/Ti/SiO_2/Si) and then was heated at 450°C for 10 min. As the desired thickness of the film was achieved, the sample was then subjected to heat treatment at 500°C for 3 h. The obtained sol–gel-derived aluminum oxide was denoted as AmAO thin film. For testing the dielectric properties of aluminum oxide thin film. The top electrode was deposited onto the surface of aluminum oxide to produce a Metal–Oxide–Metal (MIM) device.

3.3. *The structural characteristics of sol–gel-derived aluminum oxide*

The sol–gel method, being a form of soft chemistry, allows for the incorporation of a significant amount of water molecules and hydroxyl groups. The TG-DSC, FT-IR and XRD were employed to investigate properties of aluminum oxide thin film, as shown in Fig. 5. TG-DSC analysis reveals three

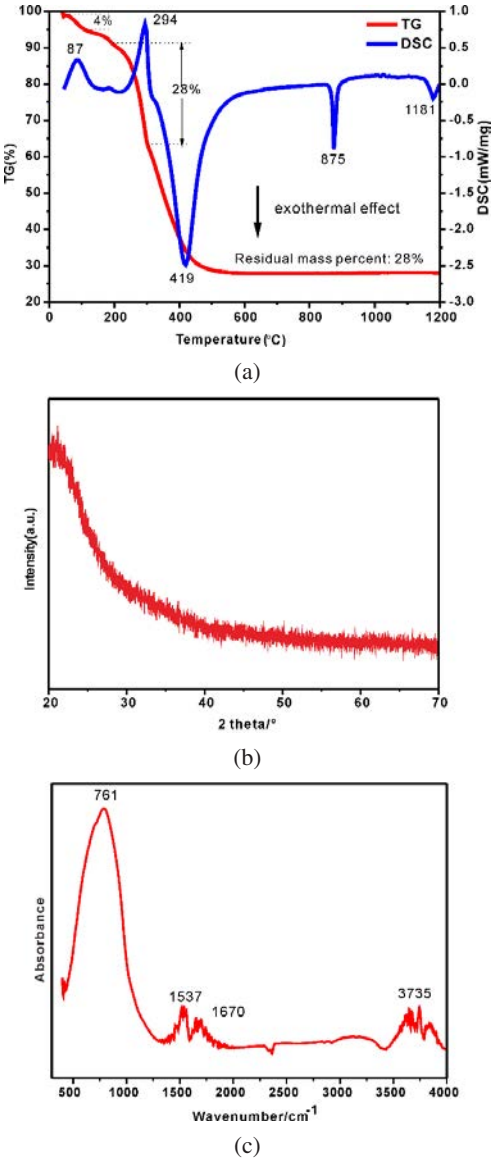

Fig. 5. The (a) TG-DSC, (b) XRD and (c) FT-IR spectra of aluminum oxide thin film.[44,45]

distinct phases based on the following temperatures (Fig. 5(a)): (a) 30–320°C, (b) 320–640°C and (c) 640–1200°C. (a) There are two exothermic peaks at 87°C and 294°C, which are attributed to desorption process of physical adsorption and chemical adsorption water molecules, respectively. The corresponding weight losses are 4% and 28%, respectively. Especially, the weight loss of 28% can be assigned to the dehydration of $Al(OH)_3$ due to the theoretical weight loss 23% for $Al(OH)_3$ dehydration. (b) Spanning the temperature range of 320–640°C, there is a wide exothermic peak. This is mainly due to the thermal decomposition of organics. (c) As the temperature rises, the sample presents two endothermic peaks at 875°C and 1181°C, which results from the transformation of amorphous aluminum oxide to γ-aluminum oxide and γ-aluminum oxide to α-aluminum oxide.

As demonstrated in 5(b), the film, treated at 500°C, holds a predominantly amorphous structure 5(c). The amorphous structure exhibits a high specific surface area which facilitates the adsorption of water molecules. Figure 5(c) shows the FT-IR spectrum of the film. In the range of 3000–4000 cm^{-1}, the peak at 3735 cm^{-1} is attributed to water molecules and hydroxyl groups.[33,43] The peak at 1670 cm^{-1} corresponds to the bending vibration peak of hydroxyl groups. It is concluded that the aluminum oxide thin film contains water molecules and hydroxyl groups. Especially, the mass ratio of physical adsorption water molecules and chemical adsorption hydroxyl groups of the film are ~4% and 28%.

4. Sol–Gel-Derived Aluminum Oxide Dielectric Capacitor

The sol–gel-derived aluminum oxide adsorbs water molecules/hydrogen groups. The adsorbed water molecules/hydrogen bond could be electrolyzed to form oxygen ions, hydrogen groups and hydrogen ions, endowing aluminum oxide with an electrolysis feature. The sol–gel-derived aluminum oxide-based dielectrics are chosen as dielectric layers and valve metals as top electrodes to structure dielectric capacitor. According to the type of dielectrics, the devices are divided into aluminum oxide capacitor and aluminum oxide-based capacitor.

4.1. *Aluminum oxide capacitor*

An aluminum oxide capacitor contains Al/Aluminum oxide oxide/Pt system, Ti/Aluminum oxide/Pt and Cu Aluminum oxide/Pt systems.

4.1.1. *Al/Aluminum oxide oxide/Pt system*

Hu *et al*.[31] revealed that the sol–gel-derived aluminum oxide-based MIM dielectric capacitor with Al top electrode showed a dramatic difference characteristic of current-electric field (I-E) measurement compared with Pt top electrode, as shown in Fig. 6(a). With Pt top electrode, the leakage current increases with voltage rising until the occurrence of breakdown. While the leakage current remains relatively stable as the voltage rises with Al top electrode, additionally, the leakage current with an Al top electrode is significantly lower than that with a Pt top electrode, and the breakdown strength increased by 79% to 465 MV m^{-1}. Hu *et al*. proposed a possible mechanism to explain this electrical behavior observed with an Al top electrode, suggesting that it could be attributed to electrochemical reactions of Al electrode. Namely, Al^{3+} ions combine O^{2-} to form Al_2O_3. However, the above conclusion is more speculative and the newly formed Al_2O_3 is not experimentally confirmed.

Chen *et al*.[46] discovered similar current–voltage characteristics compared to Ref. 31, as shown in Fig. 6(b). They first elucidated that the above phenomenon is due to anodic

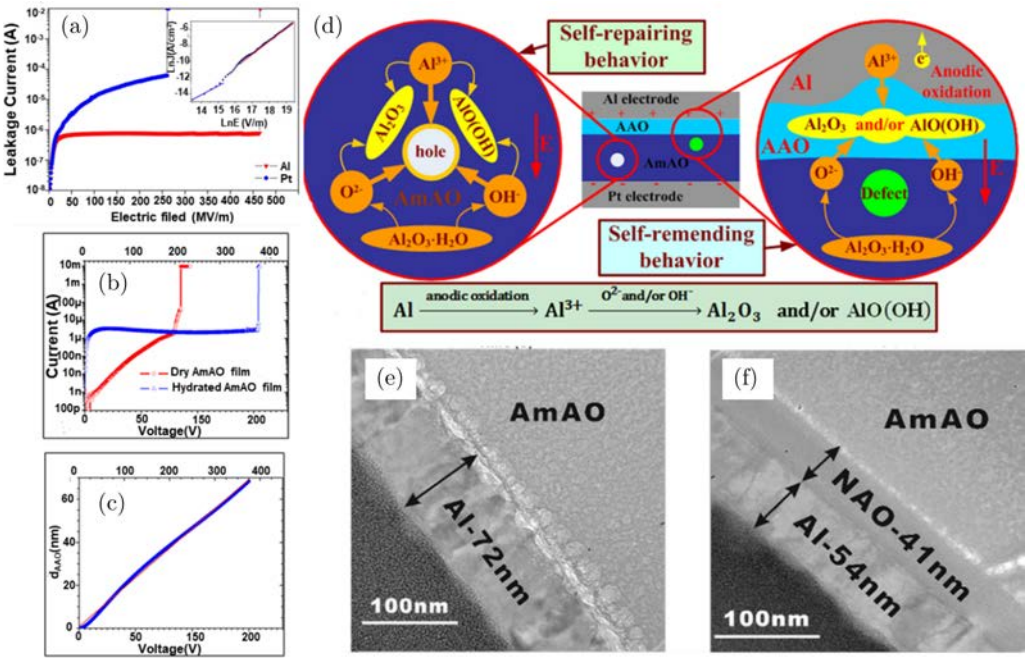

Fig. 6. (a) I-E measurements for capacitor with Pt and Al top electrodes. The inset shows ln J versus ln E curves of the device with Pt top electrodes; (b) I-V curves for dry and hydrated alumina oxide film with Al top electrode; (c) The relationship between the voltage and thickness of the newly-formed alumina film on the Al/AmAO interface; (d) Diagrammatic drawing for the self-healing effect with Al electrode; (e) TEM cross-sectional image of Al/AmAO before the applied voltage; and (f) TEM cross-sectional image of Al/AmAO after applying a constant voltage.[46]

oxidation. The Al top electrode undergoes anodic oxidation, resulting in the formation of aluminum oxide. Under an ideal circumstance, where the current efficiency of the anodic reaction is 100%, the calculated thickness of aluminum oxide linearly increases with the voltage increasing, which is a typical anodic oxidation curve (Fig. 6(c)). Meanwhile, they proposed an anodic oxidation model to illustrate the above anodic oxidation process, as shown in Fig. 6(d). Under the driving force of the electric field during the measurement, the O^{2-}/OH^- anions in the hydrated amorphous aluminum oxide film (AmAO) migrate toward the aluminum anode and oxidized the aluminum at the Al/AmAO interface region, transforming the Al^0 atoms into Al^{3+} cations and forming aluminum oxide and/or hydroxide aluminum oxide (AAO). The overall reaction can be described as shown in Fig. 6(d). The anodic oxidation process serves to repair defects present within the aluminum oxide and near its surface, subsequently enhancing the breakdown strength of the film and thereby improving the energy density of the devices. They first proposed a detailed mechanism to explain this unique phenomenon and suggested that the newly formed aluminum oxide (NAO) comprises not only Al_2O_3 but also hydrated aluminum oxide, such as AlO(OH).

The above two works of analyzing the anodic oxidation are relatively qualitative and speculative. The NAO is not confirmed definitively and the reason for the NAO enhancing dielectric properties is not clear. Su *et al.*[47] employed TEM technology and electrochemical measurements to provide quantitative explanations for the phenomenon. They definitively confirmed the existence of NAO after the application of an electric field, as depicted in Figs. 6(e) and 6(f). Meanwhile, they revealed that the resistance of NAO is 9.4×10^{12} Ω cm and the resistance of AmAO film increases from 2.4×10^8 Ω cm to 4.6×10^9 Ω cm. The significant increase in resistance is responsible for the enhancement of breakdown strength. Moreover, the growth mechanism of NAO was further explored. According to the activation energies of water molecules, physically adsorbed water ($Al_2O_3 \cdot H_2O$) and chemically bound hydroxyl groups (AlO(OH)) are determined. Depending on the thickness ratio of oxide film to aluminum layer with/without physically adsorbed water molecules, two growth mechanisms are proposed, as shown in Fig. 7. The NAO growth stems from amorphous aluminum oxide transformation and chemical reaction of aluminum electrode. Moreover, the Al/AmAO/Pt energy density increases from 2.6 to 13.9 J cm^{-3}.

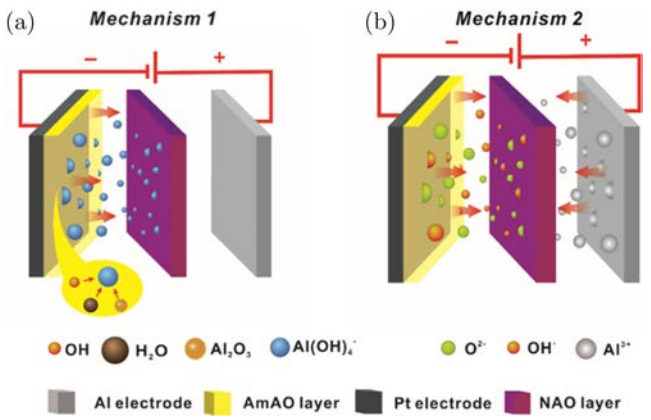

Fig. 7. Schematic for growth mechanisms of newly-formed aluminium oxide layer.[47]

4.1.2. *Ti/Aluminum oxide/Pt and Cu Aluminum oxide/Pt systems*

The electrolysis of aluminum oxide could anodic oxidized Al top electrode to form a dense aluminum oxide and further improve the dielectric properties. It could be concluded that the sol–gel-derived aluminum oxide could oxidize other valves metals, such as titanium (Ti) and copper (Cu). Su *et al.*[42,48] conducted experiments to explore the anodic oxidation reactions of sol–gel-derived amorphous aluminum oxide with other valve metals, such as titanium (Ti) and copper (Cu). For titanium/sol–gel-derived amorphous aluminum oxide system (Ti/AmAO)/Pt, 65 nm thickness Ti electrode was prepared (Fig. 8(a)). After applying an electric field, the Ti electrode was anodized to form double dielectric layers of compact TiO_2 and Al_2O_3/TiO_x under high electric field (Fig. 8(b)). The resistance of TiO_2 layer is on the order of magnitude of 10^9 Ω · cm and Al_2O_3/TiO_x layer is in the order of magnitude 10^{11} Ω · cm, which makes contributions to improving breakdown strength of up to 548 MV m^{-1} (Fig. 8(c)). The high dielectric constant of TiO_2 layer (up to 28.1) contributed to an overall dielectric constant of 15.9. The achieved energy density was as high as 20.9 J cm^{-3} at 545 MV m^{-1}. In the Cu/AmAO/Pt system, the sol–gel-derived aluminum oxide undergoes electrolysis, resulting in the production of copper oxide under high electric field conditions. The newly formed copper oxide is found to be complex, which contains Cu_2O, CuO (Figs. 8(d) and 8(e)). The high breakdown strength (425 MV m^{-1}) and improved leakage current density are achieved due to this effective system (Fig. 8(f)). The dielectric capacitors demonstrate a much higher energy density of 6.9 J cm^{-3} than that of Au/AmAO/Pt system (2.9 J cm^{-3}).

4.1.3. *Al/Aluminum Oxide-based dielectrics/Pt systems*

Aluminum oxide is capable of anodic oxidization of the valve metals to enhance the breakdown strength of the device and further improve energy density. However, the aluminum oxide exhibits a lower dielectric constant compared to $SrTiO_3$ dielectrics. Based on this, Peng *et al.*[49,50] conducted research to introduce the electrolysis property of the aluminum oxide into $SrTiO_3$ films to enhance their breakdown strength and improve the energy density. They

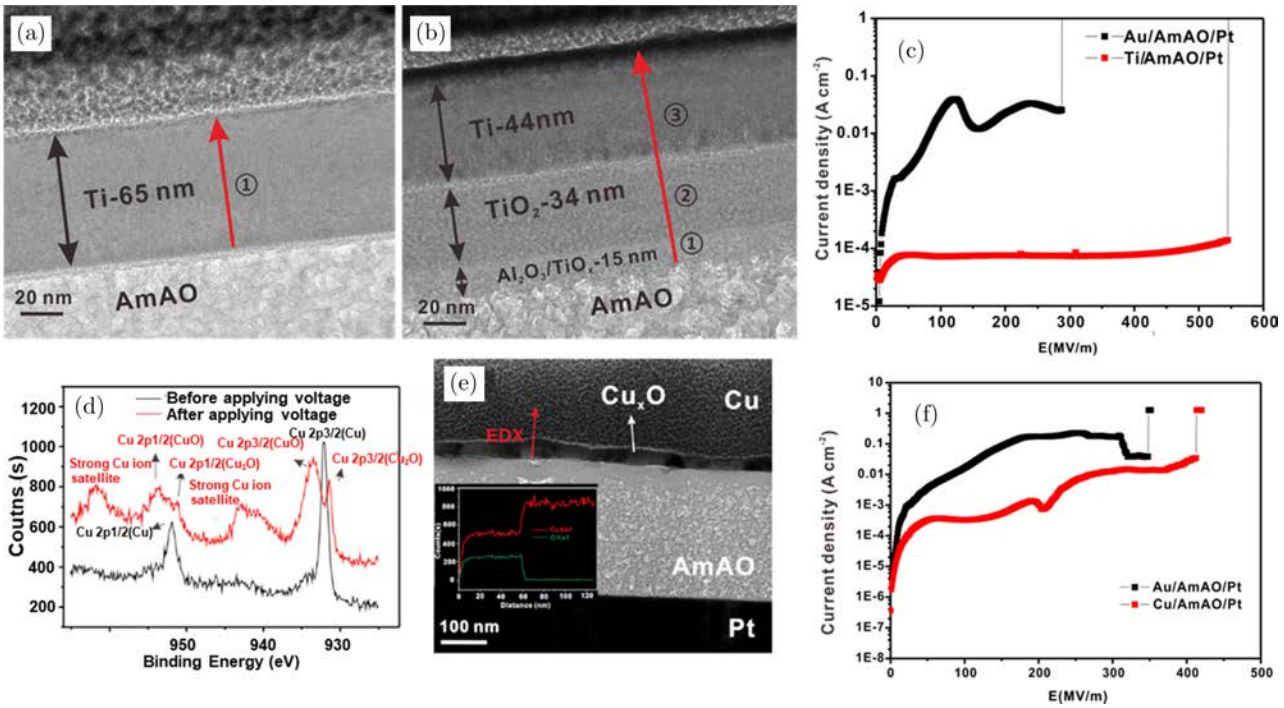

Fig. 8. TEM cross-sectional images (a) before and (b) after J-E measurement with 65 nm titanium film; (c) lnJ-E characteristics for Au/AmAO/Pt and Ti/AmAO/Pt systems; (d) The Cu 2p XPS spectra for Cu/AmAO/Pt system before and after applying voltage; (e) The TEM and EDX images of Cu/AmAO/Pt after applying electric field; (f) lnJ-E characteristics for AmAO/Pt and AmAO/Pt systems with Au and Cu electrodes.[42,48]

employed two methods to endow $SrTiO_3$ films with an electrolysis property: (a) Doping nanoAl_2O_3 into $SrTiO_3$ films (N-STO) and (b) coating sol–gel-derived aluminum oxide films onto $SrTiO_3$ films ($SrTiO_3/Al_2O_3$ laminated films). Both methods achieve high breakdown strengths, as shown in Figs. 9(a) and 9(b). The N-STO film exhibits a significantly enhanced dielectric strength of 506.9 MV/m, which is improved by 114.8% compared to the pure $SrTiO_3$ film (Fig. 9(a)). Combined with the high dielectric constant of $SrTO_3$, the energy density increases to ~19.34 J cm^{-3}. The $SrTiO_3/Al_2O_3$ laminated films were prepared by the sol–gel process with a structure of 160 nm $SrTiO_3$ layer on top of a 90 nm Al_2O_3 layer. The dielectric strength of laminated films with Al top electrodes improves from 205 to 322 MV m^{-1}. Simultaneously, the leakage current maintains the same order of magnitude (104 A cm^{-2}) until the breakdown occurs (Fig. 9(b)). Peng *et al.* proposed that the enhanced breakdown strength can be attributed to the anodic oxidation reaction, which can repair internal and/or surface defects of the films (Fig. 9(c)). The detailed process was discussed in part of "*Al/Aluminum oxide oxide/Pt system*".

5. Summary and Outlook

Electrolysis and dielectric co-existence dielectrics are a kind of new materials. Electrolysis of dielectrics can anodize valves metal to form metallic oxide achieving a self-healing effect. The newly formed metallic oxide possesses a high breakdown strength/dielectric constant and further improves energy density of dielectric capacitor. This is a simple and cost-effective method by utilizing the outstanding dielectric properties of newly formed metallic oxide. The electrolysis and dielectric co-existence dielectrics show a dramatic potential in improving energy density. This new type of dual-function aluminum oxide can be combined with flexible valve metal foils to directly construct all-inorganic flexible dielectric capacitors. By utilizing the self-repairing effect between the electrolyte properties and the valve metal, the energy-density of flexible capacitors can be enhanced. This process effectively leverages the inherent propensity of valve metal foils for oxidation, thereby transforming the disadvantage of valve metal foils' susceptibility to oxidation into an advantageous attribute when employed as electrodes. This approach circumvents the traditional fabrication methods of flexible devices of growth-transfer techniques, and significantly reduces the difficulty and cost associated with the preparation of flexible devices. Moreover, this type of dielectric material holds the potential to replace the ceramic material and electrode material in traditional multilayer ceramic capacitors, while achieving both defect self-repair within the device's internal structure and cost reduction of internal electrodes. However, the only sol–gel-derived aluminum oxide with both electrolysis and dielectric performances is discovered. The related researches also focus on sol–gel-derived

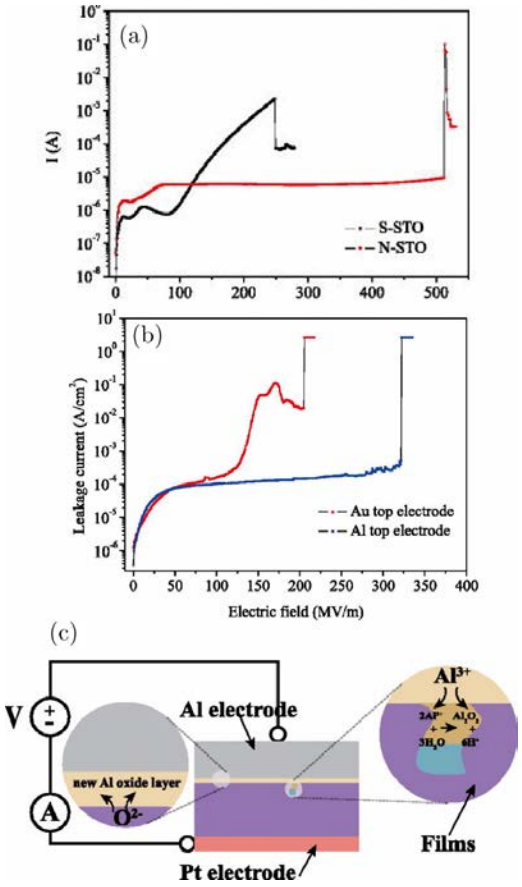

Fig. 9. E-I curves for (a) $SrTiO_3$/nanoAl_2O_3 (N-STO) and $SrTiO_3$/sol-Al_2O_3 (S-STO); (b) E-I curves for $SrTiO_3$/Al_2O_3 composites with Au and Al top electrodes; (c) Schematic diagram for self-repairing mechanism with the Al top electrode under high electric field.[49,50]

aluminum oxide which severely limits the further applications of such dielectrics. Therefore, some new electrolysis and dielectric co-existence dielectrics should be explored and widen their applications.

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