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Evolution of active species and discharge sparks in Na_2SiO_3 electrolyte during PEO process

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ABSTRACT

For the plasma electrolytic oxidation (PEO) of Mg alloy in Na_2SiO_3 electrolyte, optical emission spectroscopy (OES) was adopted to identify the active plasma species at the four stages and the evolution of the discharge sparks in the PEO process was analyzed. At the conventional anodic oxidation stage the emitting-light was correlated to the “flaws” in the oxide films. At the transition stage the active species were O_2 and H_2O. At the transition stage, the collapse and ionization of the bubble layer happened. At the plasma discharge stage, the active plasma species transited and emitted light. The main active plasma species of the micro-discharges were Na, K, Mg, H_α, O_2^+ and OH. At the arc discharge stage, the energy was not uniform and the discharge was uneven, the light intensity increased sharply, O^+ and O were excited.

1. Introduction

Na_2SiO_3 has been widely used as the main electrolyte in plasma electrolytic oxidation (PEO) process. The PEO films generated in this electrolyte exhibit excellent anticorrosion and mechanical properties [1,2]. Lots of experts have conducted a series of extensive investigations on the PEO films, such as surface morphologies [3], chemical compositions [4], micro-structures [5] and cross-sections [6]. These investigations correlated to the performance of the PEO films closely. However, all the investigations focused on the characteristics of the PEO films only. It is known that the discharging features of plasma are very important in PEO technology and have been attracting increasing attentions of many researchers [7–10]. What are the compositions of the discharge sparks in the Na_2SiO_3 electrolyte? Where are they from and how they correlate to the PEO process? The behavior of active plasma species in the micro-discharges during the PEO process could help us to answer these questions.

Optical emission spectroscopy (OES) has been widely used in the study on plasma physics [11]. It is a promising method for plasma detection without disturbing the liquid systems to be tested, such as PEO [12], glow discharge plasma electrolysis (GDPE) [13], dielectric barrier discharge (DBD) [14]. However, it has not been widely used in the PEO process. Dunleavy et al. [15] investigated the characteristics of discharge sparks events with OES. They revealed that the core possessed higher density plasma while the peripheral region possessed lower density plasma. Mecuson et al. [16] reported the line intensity of active plasma species of aluminum alloy imaged by OES. Li Wang et al. [12] investigated the breakdown mechanisms of various anodic films. The active plasma species of the micro-discharges in a series of different electrolytes were analyzed systematically by OES. The active plasma species were found to undergo dissociation, ionization, and excitation process.

In the paper, the active plasma species appeared in the plasma field in Na_2SiO_3 electrolyte at the conventional anodic oxidation stage, transition stage, plasma discharge stage and arc discharge stage were investigated. The appearance evolution of the discharge sparks at different stages was also discussed.

2. Experiment

2.1. PEO film preparation

AZ31 magnesium alloy and stainless steel were used as anode and cathod, respectively. The alloy is composed of Al 3.1074%, Mn 0.4219%, Zn 0.9075% and balance magnesium. They were polished with waterproof abrasive paper up to 2000 grit, and then degreased with acetone and alcohol, followed by rinsing with distilled water. The power supply was a self-made dc power supply with voltages of 0–1500 V and currents 0–5 A. The currents and voltages were recorded with a data acquisition system automatically. The molar ratio of Na_2SiO_3 and KOH was 2:1 and the concentration of KOH was 0.07 mol/L. Other details for the PEO film preparation have been reported in our previous studies [9,12,17].

2.2. Detection of active plasma species of the micro-discharges in the plasma field

The active plasma species of the micro-discharges generated in the Na_2SiO_3 electrolyte at different PEO stages were identified by a QE 65000 OES with a spectral resolution of 1 nm. This experiment was carried out in a dark room to avoid the inter-

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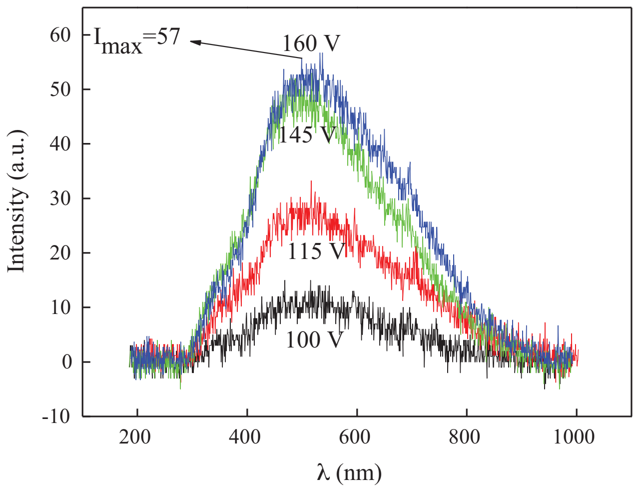

Fig. 1. OES spectra collected from samples treated in Na_2SiO_3 electrolyte at conventional anodic oxidation stage.

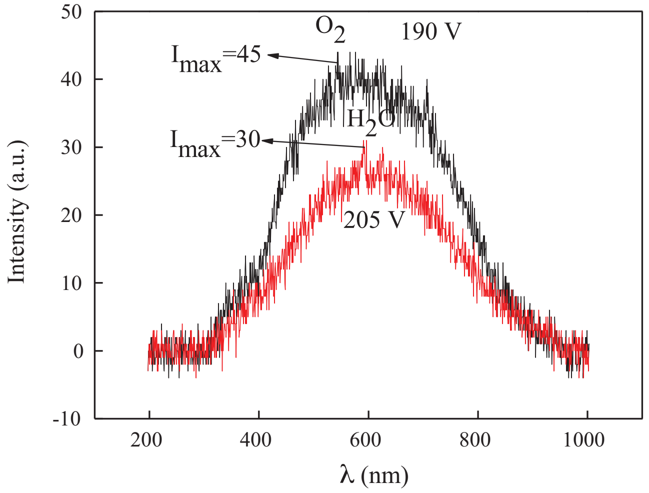

Fig. 2. OES spectra collected from samples treated in Na_2SiO_3 electrolyte at transition stage.

ference of external light. An optical fiber close to the quartz glass vessel wall of the reactor was used to collect the light emitted by the micro-discharges in the plasma field. The integration time of the spectral intensity was 1 s. The micro-discharge spectra data were recorded as soon as the voltage was applied. The details of the detection of the active plasma species have been reported in our previous studies [12,14]. The state of each species' wavelength in the spectra was confirmed by the handbook named “The Identification of Molecular Spectra” [18].

3. Results and discussion

3.1. The active plasma species produced during the PEO process

Fig. 1 shows the spectra at 100, 115, 145 and 160 V. It can be seen that the detected light intensity increased with the increasing voltage. Its value is between 10 and 57 a.u. As discussed in our previous study [12] and by other researchers [19–22], at the conventional anodic oxidation stage, the light emission could be attributed to the phenomena called galvanoluminescence (GL) and electroluminescence. Shimizu and Tajima [23] reported that the “flaws” in the oxide films resulted in the light-emitting. The “flaws” might come from the impurities on the substrate surface. They also suggested that the intensity of the GL was roughly proportional to the quantity of the “flaws” in the oxide films. That is to say, as the voltage increases, more and more “flaws” (such as micro-fissures, cracks, local regions of different compositions and impurities) occur in the oxide films, therefore, the light intensity increased gradually.

At the transition stage, the collapse and ionization of the bubble layer occurred, the collected spectra were mainly O_2 (538.00 nm) and H_2O (594.31 nm). The light intensity decreased with an increase in voltage. As shown in Fig. 2, the light intensity at 190 and 205 V were 45 and 30 a.u., respectively. Since the bubble layer on the surface of the substrate was broken down first at this stage, it needed lots of energy. So it can be inferred that the decrease of the light intensity has a different mechanism compared to that of at the conventional anodizing stage. The decrease in light intensity should be related to the energy dropping on the substrate surface. As discussed in our previous studies [9,24], at this stage, the current density decreased sharply with the increasing voltage. The current density can reflect the energy on the surface of the substrate to some extent. As lots of energy was used to break down the bubble layer, the energy might be converted into heat or other forms, so the light intensity decreased with the voltage.

Fig. 3 presents the OES spectra collected from the Na_2SiO_3 electrolyte at plasma discharge stage. As shown in Fig. 3(a) and (b), the species of Na (589.01 nm) appeared as the voltage increased to 260–280 V. When the voltage increased to 290 V, K began to be excited in the plasma field (as shown in Fig. 3(c)). As the voltage increased to 300 V, Mg (519.40 nm) and O_2^+ (383.05 nm) also began to be excited. The spectra were similar as the voltage was kept between 300 and 335 V (as shown in Fig. 3(d)). When the applied voltage reached 370 V, as shown in Fig. 3(e), after the metal species (Na, K and Mg) were excited, OH (309 nm) and H_α (656.32 nm) also began to be excited. As discussed in our previous studies, the order of the excited active plasma species depends on the energy that the orbit transition of the species needed [12]. At the plasma discharge stage, the energy in the plasma field would be increased with the voltage increase. So the metal elements were excited first, they needed lower excited energy than that of O and H elements.

Fig. 4 shows the maximum light intensity at different PEO stages. At stage 1, the light intensity increased with the increasing voltage, the emission light could be ascribed to the “flaws” in the oxide films. So the increased intensity was roughly proportional to the concentration of the “flaws” in the films. At stage 2, as the bubble layer broken down, followed by the breakdown of the dielectric barrier layer, most of the energy on the surface of the substrate was used to break down the two layers. Therefore, the current density sharply decreased at this stage, so is the energy. Thus, the light intensity decreased with the increasing voltage. At stage 3, the plasma discharge occurred, it can be seen that the light intensity increased with the increase in voltage. At this stage, the active plasma species were excited in the plasma field, they underwent dissociation, ionization, and excitation process [12]. The conversion of the energy would occur in different forms. The energy on the surface of the substrate was increased with the increase in voltage. So the discharge became more and more intense as the voltage increased. The highest light intensity at different voltages could reflect by the intensity of Na. That is to say, with the increase of the voltage, the energy increased, more and more Na elements were excited, so its light intensity increased with the increase in voltage at stage 3.

When the PEO process entered the arc discharge stage, the discharge sparks would concentrate in a few local areas (as shown in Fig. 5(g)). The sparks were dazzling and followed with the explosion sound. Thus, the light intensity at this stage increased sharply (as shown in Fig. 6). The highest intensity could change from 1500 to 60,000 a.u. In addition, the current density would decrease with the increased voltage because of the uneven discharge and the energy consuming mainly as heat. The electrolyte temperature increased quickly at this stage and lots of steam generated on the surface of the samples. Most of the researchers had reported that the energy

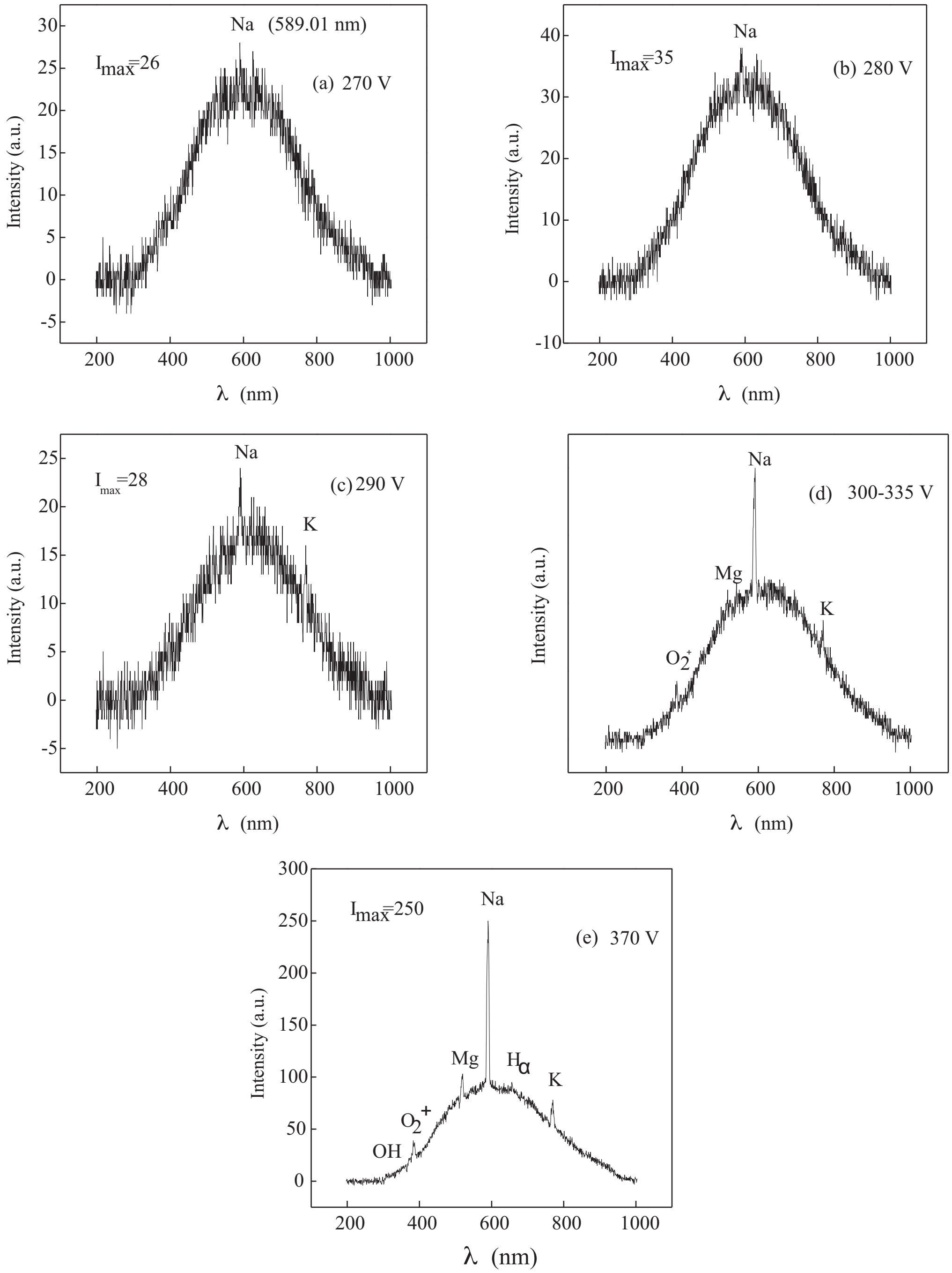

Fig. 3. OES spectra collected from samples treated in Na_2SiO_3 electrolyte at the plasma discharge stage.

efficiency is low at this stage and the PEO films could be destroyed [9,25]. As some local energy was very high, lots of O^+ (820.02 nm), OI (448.72 nm) began to be excited. They were not found at the plasma discharge stage.

3.2. The discharge sparks' evolution of PEO process in Na_2SiO_3 electrolyte

As shown in Fig. 5, the appearance of the sparks during the PEO process had gone through significant changes. For the purpose of the sparks, combining the author and other experts' studies [9,12,26], the sparks' evolution could be divided into three stages. At the first stage, a small amount of white sparks, which were mobile and non-continuous, appeared (as shown in Fig. 5(a)). At this stage, the bubble layer was broken down first, followed by the breakdown of the dielectric barrier layer. H_2O and O_2 were the main active species excited in the bubble layer, and Na may not be excited or be excited little, so the appearance of the sparks was white. At the second stage, with the increase of the voltage (as shown in Fig. 5(b)–(d)), the energy on the surface of the substrate increased, Na and K were excited in the plasma field, the sparks' color tended to be yellow, and the color became deeper with the increasing voltage. The size of the sparks increased and the density reduced gradually with the voltage. The appearance of the sparks was mainly dominated by the flame reaction of Na element. At the third stage, when the applied voltage increased to 335–370 V, the energy continued to increase. The amount of the excited metal elements became more and more, so the light inten-

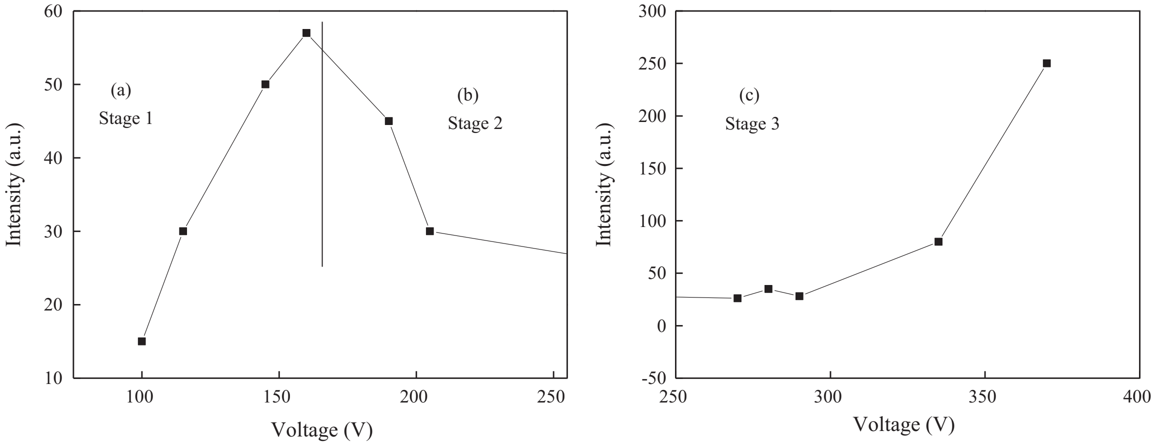

Fig. 4. The maximum intensity at different PEO stages (a) Conventional anodizing (b) Transition (c) Plasma discharge.

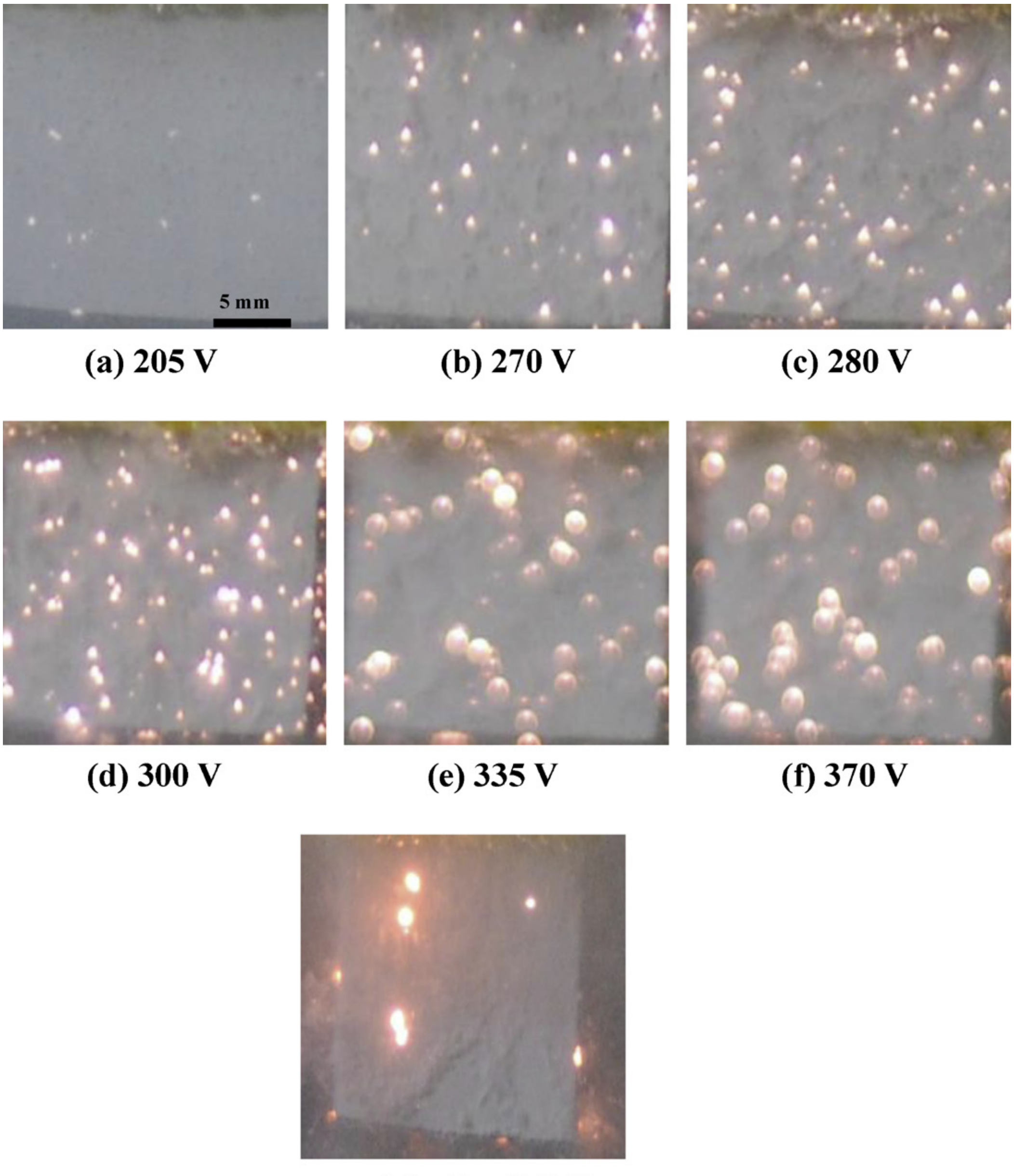

Fig. 5. The evolution of the discharge sparks' appearance at different PEO stages in Na_2SiO_3 electrolyte (a) The transition stage (b)–(f) The plasma discharge stage (g) The arc discharge stage.

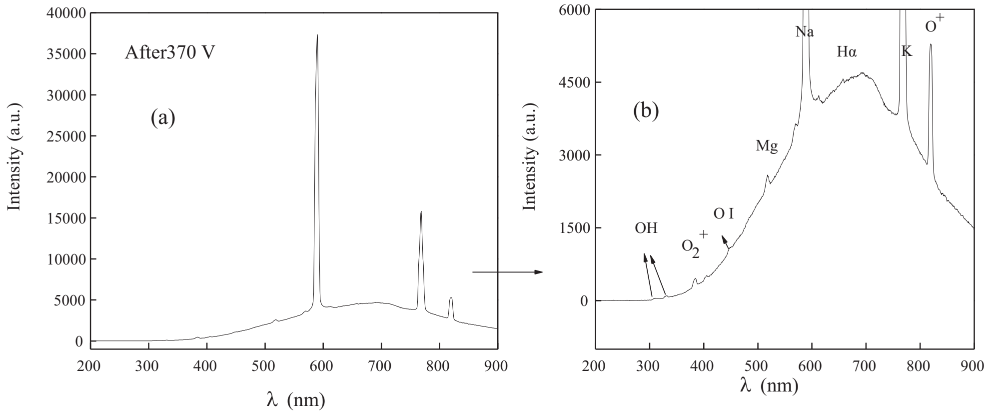

Fig. 6. OES spectra collected from samples treated in Na_2SiO_3 electrolyte at the arc discharge stage after 370 V (a) The overall graph (b) The enlarged graph.

sity of the Na increased with the increase in voltage (Fig. 4). Since H_α, O_2^+ and OH began to be excited (as shown in Fig. 5(e) and (f)), so the color of the sparks seemed to be not uniform and pure. After 370 V, the arc discharge occurred, the discharge is not uniform (as shown in Fig. 5(g)). Therefore we should avoid this stage during the PEO process. As discussed above, the size, density and color variation of the sparks may be ascribed to the changes of the number and type of the active plasma species, the growth of the films and the applied energy.

4. Conclusions

For the plasma electrolytic oxidation (PEO) of Mg alloy in Na_2SiO_3 electrolyte, the mechanisms of light emission were different at different stages. At the conventional anodizing stage, the light emission could be ascribed to the “flaws” in the oxide films, which leaded to the GL and the variation of the light intensity. At the transition stage, the bubble layer and dielectric barrier layer were broken down, the bubble layer ionized and collapsed. At this stage the active species were mainly O_2 and H_2O. At the plasma discharge stage, lots of metal elements related H and O elements were excited in the plasma field. The variation of the spark size, density and color at different PEO stages may be ascribed to the changes of the number and type of the active plasma species, the growth of the films and the applied energy.

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