

# Behavior of acid species during heat treatment and re-anodizing of porous alumina films formed in malonic acid

I. Vrublevsky · A. Jagminas · S. Hemeltjen · W. Goedel

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**Abstract** In the present work infrared spectroscopy, photoluminescence spectral measurements and the potentiodynamic technique for studying the effect of treatment temperature on compositional and electronic properties of malonic acid alumina films were used. In the course of our studies, it has been proven that heat treatment of malonic acid films at temperatures from 250 up to 400 °C leads to considerable changes in the photoluminescence properties and voltammetric response during their potentiodynamic re-anodizing. We suggest that defects, such as electron traps, in this type of porous anodic films are caused by the atoms of hydrogen (one or two) escaping from the CH<sub>2</sub> groups of the malonic acid species as a result of the heat treatment. The sites of such defects provide pathways for easy electron migration under a high electric field increasing electroconductivity of anodic alumina films. On the contrary, no structural defects responsible for enhanced electroconductivity are observed during thermal splitting of oxalate groups in the oxalic acid alumina films.

**Keywords** Aluminum · Anodizing · Anodic alumina · Electroconductivity · Malonic acid

## Introduction

The uniqueness of aluminum among valve metals lays in the possibility to produce both thin-barrier-type and thick-porous-type oxide films under certain anodizing conditions. The composition of anodizing solution is the primary determinant of whether the film will be barrier or porous. The most widely used solution for porous anodizing is dilute sulfuric acid. Since the past, anodizing in oxalic acid solutions was used for hard anodizing of aluminum [1]. In the past decade, oxalic acid alumina films grown under specific anodizing conditions [2, 3] and possessing high-ordering honeycomb morphology became extremely popular as templates for the synthesis of various nanometer-scaled materials.

More than half a century ago, Kape [4] suggested the use of aqueous solutions of malonic acid in aluminum anodizing over a wide range of concentrations indicating excellent hardness and corrosion resistance of these films, although it was later not found to be widely applied in practice. Recently, Ono et al. [5] and, more recently, Lee et al. [6] reported the use of malonic acid solutions for high-ordered alumina film formation, therefore extending the potential applications of alumina templates for future nanotechnology.

As known, alumina films grown in oxalic and malonic acid solutions contain the species derived from the anions of these acids [7]. During film growth, these species migrate inward the barrier layer at a slower rate than O<sup>2-</sup> and, hence, do not reach the metal/oxide interface [8]. The increase in the bath temperature and in the anodizing

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I. Vrublevsky (✉)  
Department of Micro and Nanoelectronics, Belarusian  
State University of Informatics and Radioelectronics,  
6 Brovka str,  
Minsk 220013, Belarus  
e-mail: nil-4-2@bsuir.edu.by

A. Jagminas  
Institute of Chemistry,  
A.Goštauto 9,  
01108 Vilnius, Lithuania

S. Hemeltjen · W. Goedel  
Institut für Chemie, Technische Universität Chemnitz,  
Chemnitz 09107, Germany

current results in greater incorporation of carboxylate ions [9] acting as photoluminescence (PL) centers [10]. According to a recent study, the composition of films grown in 0.4 M oxalic and 0.3 M malonic acid at 20 °C and 0.5 A dm<sup>-2</sup> can be described as Al<sub>2</sub>O<sub>3</sub>·0.025Al<sub>2</sub>[(COO)<sub>2</sub>]<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>·0.014Al<sub>2</sub>[CH<sub>2</sub>(COO)<sub>2</sub>]<sub>3</sub>, respectively [11]. These descriptions, however, can be sometimes misleading since the structure of incorporated species, especially at higher voltages, showed some variation with the increase in the depth of alumina walls due to the decomposition of carboxylate ions taking place in the barrier layer under the influence of high electric field [12]. Consequently, oxalic acid alumina films have two excitation maxima in PL spectrum that has been related with the incorporation of oxalate anions C<sub>2</sub>O<sub>4</sub><sup>2-</sup> in the outer layers and separated carboxylates COO<sup>-</sup> in layers deeper than 10 nm [13, 14]. It is notable that the thickness of alumina walls and the barrier layer with incorporated ‘structural’ ions is about 90% for oxalic acid films [15]. Furthermore, the electrical properties of the barrier layer with incorporated acid anions are quite different from those of pure Al<sub>2</sub>O<sub>3</sub> because the impurities located in the dielectric film may substantially reduce the barrier height for migration of charge carriers. In 1965, Schmidlin modeled the metal/insulator/metal junction for electron tunneling, showing that a cationic impurity located in the dielectric film volume of 1,000 nm<sup>3</sup>, where the barrier thickness ~10 nm, can increase the current through the barrier by an order of magnitude [16] through a thermally activated hopping [17].

Thermodynamically stable Al oxide has a band gap of width more than 3 eV [18], and therefore, such material belongs to dielectrics. However, owing to point defects, a band gap of anodic alumina possesses a set of local states or electron traps. As stated, the presence of such electron traps provides pathways for easy electron migration under the high electric field. Heat treatment of porous alumina films such as those formed in malonic or oxalic acids may lead to the decomposition of incorporated acid anions with structural defects emerging. Therefore, this can be the reason for an electron current growth under high electric field as a result of the injection of charge carriers from electrodes and the presence of structural defects in the bulk.

This work was aimed to study the behavior of malonic acid species during heat treatment and re-anodizing of porous alumina films. As has been shown earlier shown in [19], the simple method to create high electric field and reinforce it further in the barrier layers of porous films is a re-anodizing technique in a barrier-type electrolyte under linear sweep potential.

For anodizing the aluminum, we used malonic and oxalic acid solutions because of the considerable differences between them in the character of bonds in carboxyl groups (–COOH). For instance, this difference shows in

different melting temperatures for these acids. Therefore, one can expect that, under heat treatment, the incorporated anions of malonic and oxalic acids will behave in different ways.

In the present work, infrared (IR) spectroscopy, photoluminescence spectral measurement, and electrochemical technique were used to study the effect of treatment temperature on the composition and conductivity of malonic acid alumina films.

## Experimental

Two kinds of aluminum foil, e.g., high purity (99.999 at.%) and 25.0-μm thick, and 99.45 at.% purity and 10.0-μm thick, respectively, all purchased from Alfa Aesar, were used in our experiments. Ten-micrometer-thick aluminum sheets were anodized from both sides in a 0.8 M malonic acid solution (H<sub>4</sub>C<sub>3</sub>O<sub>4</sub>) under constant voltage of 80 V until all aluminum was wasted (about 12 h). During anodizing, the electrolyte was vigorously stirred and its temperature was kept constant at 18±0.1 °C with the Thermo Haake DC10 thermostat. After anodizing in malonic acid electrolyte, the anodic alumina films appeared almost transparent and of light gray color. Twenty-five-micrometer-thick aluminum sheets were anodized from both sides in 0.3 M oxalic acid solution (COOH)<sub>2</sub> under constant voltage of 40 V until aluminum was wasted (about 1.5 h). The films formed in this electrolyte appeared to be transparent with a light golden tint.

Aluminum foil of 99.999 at.% (Alfa Aesar) purity and 25.0-μm thickness was used in re-anodizing experiments.

The cross-sections of two-sided porous alumina films formed electrochemically in oxalic and malonic acids were studied using a scanning electron microscope JOEL 840A (SEM).

Infrared data of porous alumina films were taken using the Bruker IFS 48 FTIR spectrometer in the transmission mode. The photoluminescence measurements were taken on a Perkin Elmer fluorescence spectrophotometer. Where indicated on the plots, the specimens were heat treated under normal air conditions for 2 h.

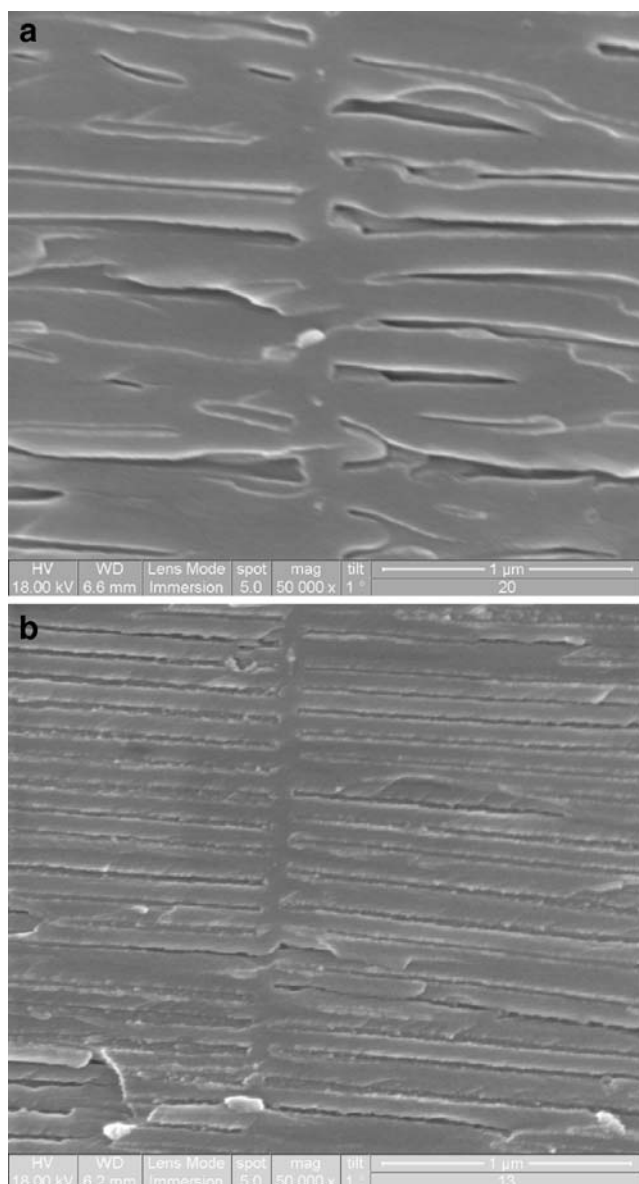
Re-anodizing of the specimens, as-grown and after heat treatment, was conducted in a barrier-type solution composed of 0.5 M H<sub>3</sub>BO<sub>3</sub> and 0.05 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> at 18 °C. Voltammetric behavior of anodized specimens was studied using the programmable potentiostat/galvanostat PI-50-1.1 at 20 mV s<sup>-1</sup> potential sweep rate mode. For these experiments, porous alumina films were manufactured by anodizing aluminum foil in oxalic acid at 35 V and in the malonic acid solution at 24 and 32 V. The data were recorded on a PC using the data acquisition card and home-written software. These experiments were performed in a

one-compartment three-electrode cell equipped with a graphite counter electrode and the Ag/AgCl, KCl<sub>sat</sub> reference electrode connected with the cell through an agar-agar/salt bridge. The reproducibility of re-anodizing measurements was checked by three repeated experiments.

All solutions for our experiments were prepared from deionized water and reagent grade chemicals.

## Result and discussion

Figure 1 shows SEM cross-sections of two-sided porous alumina films formed in malonic (Fig. 1a) and oxalic



**Fig. 1** SEM images showing cross-sections of porous alumina films formed by two-sided anodizing in malonic acid at 80 V (a) and oxalic acid at 40 V (b)

(Fig. 1b) acid electrolytes. The films formed in malonic acid show a disordered pore structure. An ordered enough nanoporous array with a close-packed structure is observed for oxalic acid film.

It is well known that physical properties of anodic alumina films are directly associated with their structure, which can be changed by further heat treatment [20]. The set of IR transmission spectra for as-grown and heat treated malonic acid alumina films are presented in Fig. 2. Double peaks centered at 1,564 and 1,475 cm<sup>-1</sup> in these spectra indicate the presence of carboxyl groups in the anodic oxide films. These peaks are attributed to the asymmetric and symmetric stretching vibrations of carboxylate ions, and the difference in their wave numbers suggests a bridging-bidentated coordination of oxalate groups with aluminum cations [21]. As shown in Fig. 2a, the absorption peak centered at 1,475 cm<sup>-1</sup> starts decreasing for films heat treated above 220 °C, while another absorption peak at 1,564 cm<sup>-1</sup> remains unchanged. After heat treatment at 600 °C, the absorption peak at 1,475 cm<sup>-1</sup> drops abruptly. Furthermore, the intensity of absorption band centered at 2,339 cm<sup>-1</sup> associated with carbon dioxide for films heated up to 300 °C remains almost constant, while after the heat treatment at 500 °C and above, the absorption band grows up rapidly (Fig. 2, inset a).

As demonstrated in Fig. 2, the absorption of COO<sup>-</sup> groups by symmetric stretching vibrations in oxide films heat treated at 220 and 300 °C weakens compared with the absorption in as-grown film. At the same time, the absorption of COO<sup>-</sup> groups by asymmetric stretching vibrations remains unchanged. Furthermore, a noticeable absorption at 2,339 cm<sup>-1</sup> (Fig. 2, inset b), linked with carbon dioxide, is not observed. Therefore, under such heat treatment, the composition of carboxyl groups remains unchangeable, although the bonds in such groups change owing to their surrounding in molecule. We can suggest that the change in infrared spectra of malonic acid films is linked with the changes in the composition of methylene group (CH<sub>2</sub>).

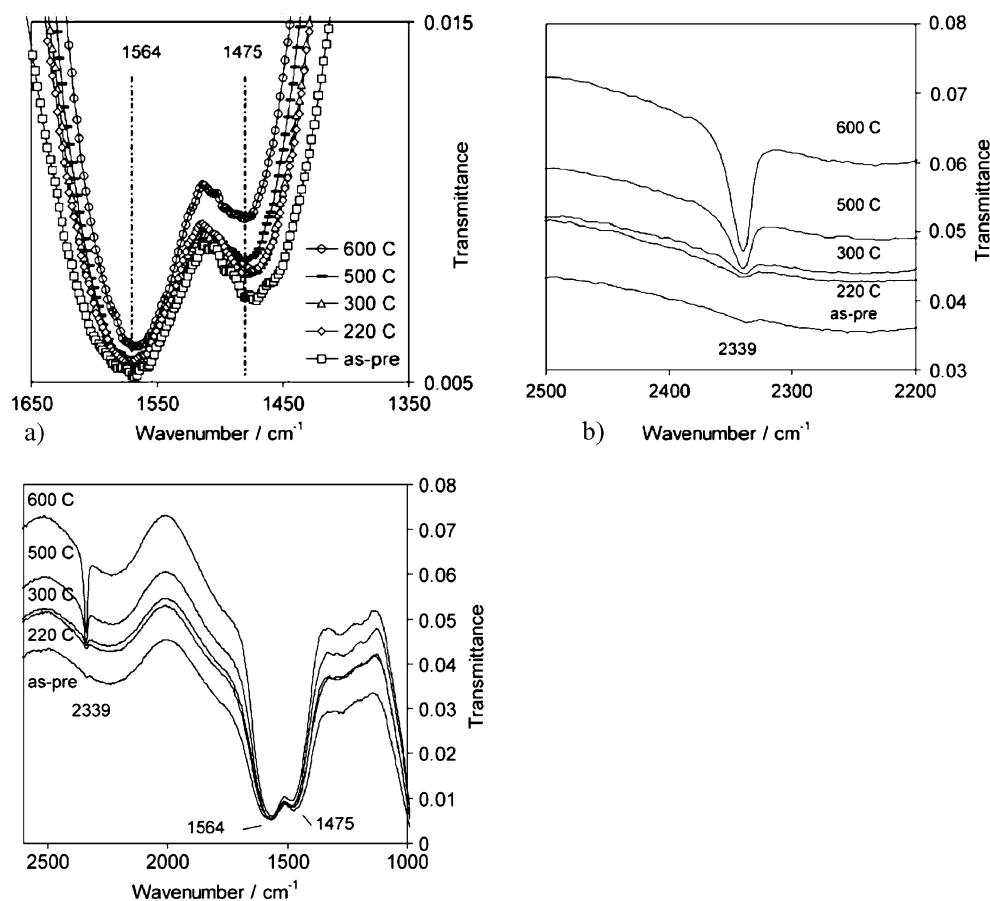
In heat treated anodic films at 500 °C and above, a noticeable decrease in absorption band centered at 1,564 cm<sup>-1</sup> is observed. At the same time, a sharp increase in absorption of carbon dioxide at 2,339 cm<sup>-1</sup> is noticed implying that, in this case, splitting of malonic acid species as a result of heating takes place:



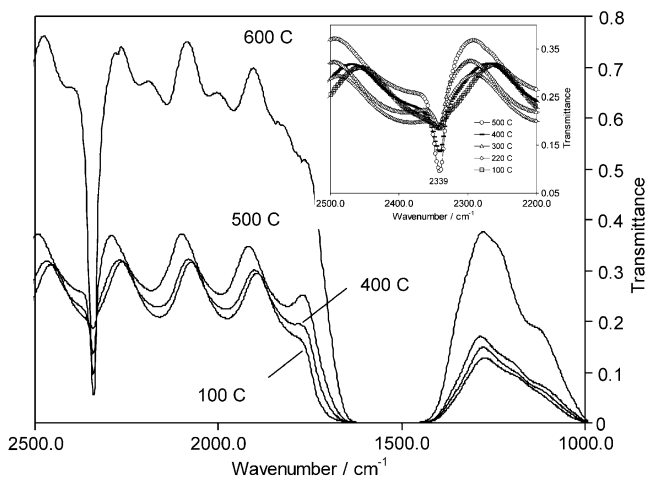
The analysis of IR spectra can be helpful in explaining the behavior of current–potential ( $j_a$  vs.  $\varphi$ ) plots during re-anodizing of heat treated anodic films in the barrier-type electrolyte.

To compare with the malonic acid alumina films, the IR spectra of oxalic acid alumina films were recorded and

**Fig. 2** Infrared transmission spectra of the malonic acid alumina films heat treated at different temperatures. *Inset a* shows infrared transmission spectra ranged from 1,650 to 1,350  $\text{cm}^{-1}$  for malonic acid alumina films heat treated at different temperatures; *inset b* shows infrared transmission spectra ranged from 2500 to 2200  $\text{cm}^{-1}$  for malonic acid alumina films heat treated at different temperatures

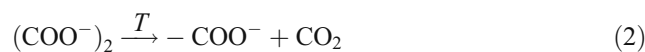


analyzed, too. Oxalic acid as well as malonic acid consists of two carboxyl groups ( $-\text{COOH}$ ). The set of IR transmission spectra of the oxalic acid alumina films shown in Fig. 3 was recorded between 2,600 and 1,000  $\text{cm}^{-1}$  after heat treatment under normal air conditions at different temperatures. It is remarkable that the oscillations observed



**Fig. 3** Infrared transmission spectra of the oxalic acid alumina films heat treated at different temperatures. *Inset* shows infrared transmission spectra ranged from 2,500 to 2,200  $\text{cm}^{-1}$  for oxalic acid alumina films heat treated at different temperatures

in all anodic alumina films spectra are due to the Fabry–Perot effect. All spectra show an absorption band centered at 2,339  $\text{cm}^{-1}$ . Emerging of the absorption band with its peak in the vicinity of 2,339  $\text{cm}^{-1}$  was attributed to  $\text{CO}_2$  [22]. Having compared the IR transmission spectra in Fig. 3, we could see that the peak of  $\text{CO}_2$  starts increasing at 400  $^\circ\text{C}$ . A temperature-related sharp increase in the absorption peak is an evidence of an increasing  $\text{CO}_2$  content in the heat treated oxalic acid alumina films. The higher the treatment temperature, the stronger the absorption band for  $\text{CO}_2$  observed in IR spectra (see inset in Fig. 3). We can conclude that the treatment above 400  $^\circ\text{C}$  results in splitting of oxalic acid species accompanied by  $\text{CO}_2$  emission as per reaction 2:



For an oxalic acid alumina film heat treated at 600  $^\circ\text{C}$ , the transmission intensity rises sharply. This is the evidence of changes in the alumina film composition, which should not be related to the film amorphous structure but to the total thermal decomposition of all oxalate anion groups in films. The amorphous structure of anodic alumina films in its turn starts transforming to crystalline at temperatures higher than 800  $^\circ\text{C}$  [23].

The voltammograms for as-grown and heat treated malonic acid alumina films formed at 24 V (a) and at 32 V (b) during re-anodizing in the solution of 0.5 M H<sub>3</sub>BO<sub>3</sub>+0.05 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> are shown in Fig. 4. As can be seen from this figure, the *j<sub>a</sub>* vs. *φ* curves of as-grown malonic acid alumina films formed at 24 and 32 V differ noticeably. First, for heat treated films formed at 24 V, the current jumps at the initial region, while for heat treated films formed at 32 V, only current growth takes place. Second, for the as-grown film formed at 24 V, the current curve shows a knee point when re-anodizing voltage reaches formation voltage, while for another film (32 V), a smooth current growth without knee point is observed. We suggest that these differences evidenced the structural changes in anodic oxide film caused by higher electric field strength taking place in case of anodizing at 32 V. As has

been shown in [24, 25], the anodizing voltage is an important characteristic for porous alumina film formation. When anodizing voltage exceeds a certain threshold, the change in film growth mechanism occurs. After this, a jump of electric field in the barrier layer of porous film is observed.

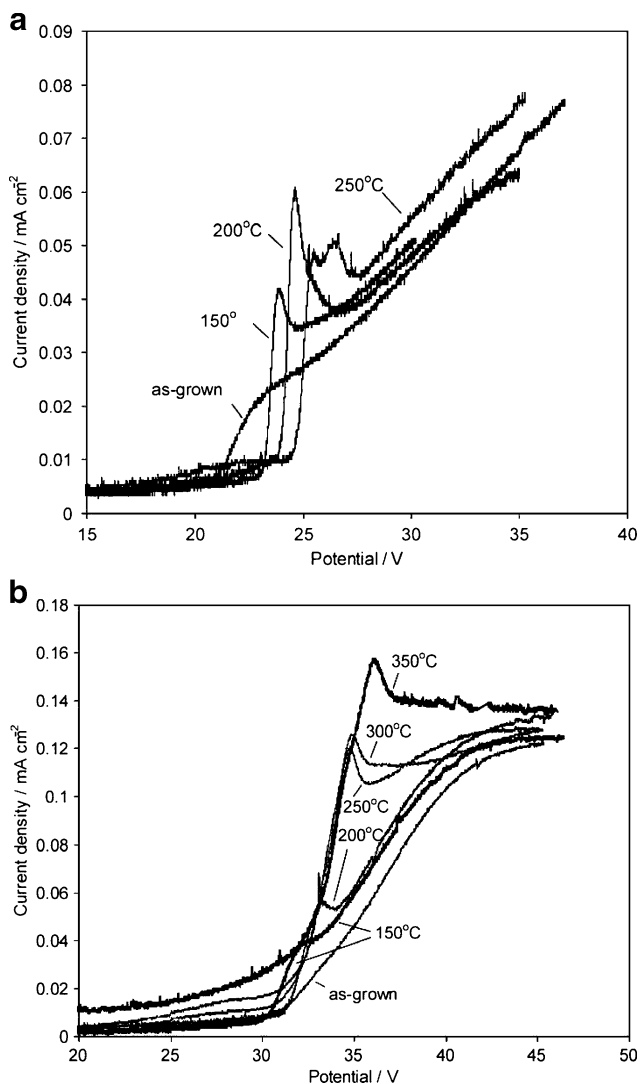
As it is known, malonic acid belongs to the group of dicarboxylic acids and has the following structure:



As can be seen, malonic acid consists of two carboxyl groups (–COOH) and a methylene one. Both carboxyl groups are strongly polarized. Oxygen in the carbonyl group shifts the electron density from carbon, and this leads to strengthening of polarization of the carbon–oxygen bond and occurrence of a partially positive charge on carbon. This positive charge in its turn shifts the electron density from the hydroxyl group to the carbon atom. Electron density displacements observed in the carboxyl group are presented in Fig. 5.

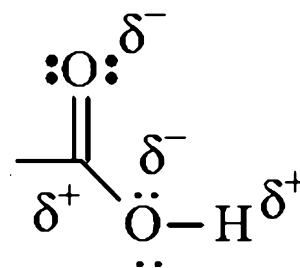
The carbon of carboxyl group will attract the electrons from the carbon of methylene group because of its partially positive charge. In malonic acid, the CH<sub>2</sub> group is under the influence of two carboxyl groups and their effect is summed up. As a result, the mobility of atoms of hydrogen in the methylene group increases, thus weakening the carbon–hydrogen bond. Therefore, any external impact such as heating or high electric field may result in the hydrogen atoms escaping. In [26], it has been demonstrated that thermal hydrogen atoms are capable of breaking carbon–hydrogen bonds in several organic compounds. The investigators found that, whereas  $\gamma$ -rays break both carbon–carbon and carbon–hydrogen bonds in malonic acid, malonamide, methyl malonic acid, and methyl malonamide, hydrogen atom bombardment of these compounds results in carbon–hydrogen bond breakage only.

Summing up, we suggest that the methylene group (CH<sub>2</sub>) of the malonic acid species can lose one or two hydrogen atoms under high electric field during re-anodizing in the barrier-type electrolyte. This brings a negative charge on the atom of carbon in the methylene group as two electrons of the hydrogen atom are left. The

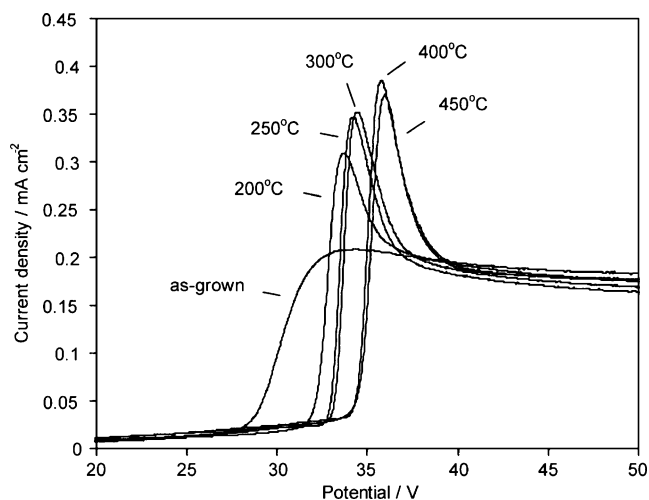


**Fig. 4** Voltammograms of heat treated porous alumina films formed in malonic acid at 24 V (a) and at 32 V (b) during re-anodizing in solution of 0.5 M H<sub>3</sub>BO<sub>3</sub>+0.05 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>

**Fig. 5** Shifts of electron density in a carboxyl group







**Fig. 6** Voltammograms of heat treated porous alumina films formed in oxalic acid at 35 V during re-anodizing in a solution of 0.5 M  $\text{H}_3\text{BO}_3 + 0.05$  M  $\text{Na}_2\text{B}_4\text{O}_7$

joined electrons may leave such atom of carbon under high electric field. As a result, this site behaves as an electron trap and can trap migrating electrons again. Consequently, sites like these may provide pathways for easy electron migration in the anodic oxide film under high electric field and increase conductivity. This assumption is in agreement with the fact that a remarkable current growth is observed after the end of transient process when re-anodizing voltage exceeds the formation voltage.

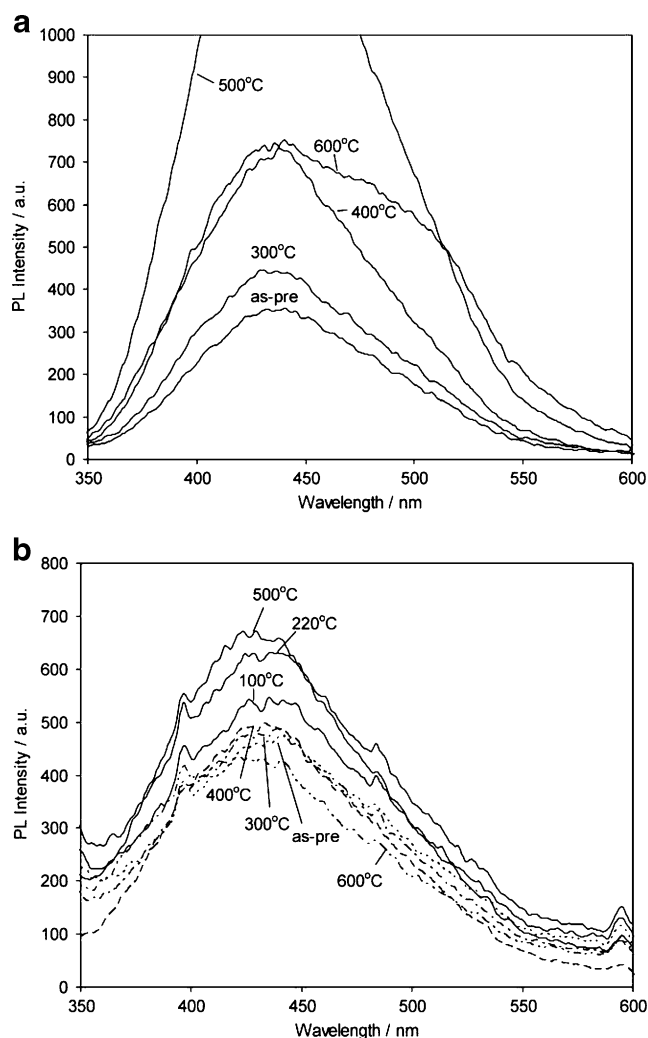
The  $j_a$  vs.  $\varphi$  plots for porous alumina films heat treated at 150 and 200 °C during re-anodizing (Fig. 4b) remained as the plot for as-grown film except for the relatively short initial region, where the current growth rate is considerably higher and the current reaches a transitional maximum. Nevertheless, after a short decay of the current–potential curve, further potential increase copies the run of the curve typical of the as-grown film.

The main feature of  $j_a$  vs.  $\varphi$  curves (Fig. 4b) is that the transient maximum observed in the initial region of the potential sweep is related to a certain amount of negatively charged carbon atoms emerging as a result of the escape of a hydrogen atom from the methylene group ( $\text{CH}_2$ ) in malonic acid species. At a higher temperature, approximately 200 °C, the mobility of the hydrogen atoms is higher, and as a result, more carbon atoms with excessive electrons appear in anodic oxide. Therefore,  $j_a$  vs.  $\varphi$  curve demonstrates a relatively high transitional maximum. It is worthy to note that the height of the transitional current maximums for films heat treated at 150 and 200 °C is more than twice lower than the saturation current for the as-grown film.

Heat treatment of porous films at 250 and 300 °C leads to substantial changes in the behavior of anodized specimens in the tetra-borate solution at the initial period of

potential sweep (Fig. 4b). In this case, we can observe a noticeable jump of the transitional current maximums. A higher transitional current maximum belongs to the film heat treated at 300 °C. This effect can be explained by the assumption that, in the methylene group ( $\text{CH}_2$ ) of malonic acid, the hydrogen atoms have different bond energy with carbon: one has higher bond energy (sigma bond), the other a lower bond energy (pi bond). For the hydrogen atoms having lower carbon–hydrogen bond energy, the bond is broken at 250 °C. Hence, though the temperature is increasing from 250 to 300 °C, the shape of  $j_a$  vs.  $\varphi$  plots remains unchanged. It is in agreement with the results of IR spectroscopy, which demonstrate the absence of carbon dioxide in films heat treated at temperatures discussed above.

The heat treatment at 350 °C causes another transitional current maximum (see Fig. 4b). We assume that, in this case, the carbon–hydrogen bond, which has a higher energy



**Fig. 7** Photoluminescent spectra for oxalic acid (a) and malonic acid (b) alumina films heat treated at different temperatures under a 330-nm excitation

in the methylene group ( $\text{CH}_2$ ), is also broken, bringing additional negatively charged carbon atoms, responsible for the growth of the electrical conductivity. Having reached its maximum followed by a short decay, the current curve enters the saturation region, which is absolutely identical to that for the as-grown film. This identity may be explained by the escape of two hydrogen atoms from the methylene groups described earlier. Therefore, further increase in electric field during re-anodizing does not cause changes in the composition of malonic acid species and defects but leads to further electronic current growth.

Figure 6 shows voltammograms of heat-treated porous alumina films formed in oxalic acid at 35 V during re-anodizing in a barrier-type electrolyte. It can be seen from this figure that the  $j_a$  vs.  $\varphi$  plots for porous alumina films heat treated from 200 to 450 °C behave in the same way during re-anodizing in the barrier-type electrolyte. Therefore, thermal splitting of the oxalic acid anions at 400 and 450 °C does not result in structural defects responsible for the electron current growth.

Photoluminescence measurements are known to provide information regarding the electronic structure of anodic oxide. Thus, comparing the influence of the treatment temperatures on the photoluminescence properties of malonic and oxalic acids alumina films may be of interest. The presence of luminescent centers in the anodic oxide films is accounted for oxygen vacancies and acid impurities incorporated into them [27].

Figure 7a shows the photoluminescent spectra of oxalic alumina films heat treated at different temperatures under a 330-nm excitation. A broad band centered at about 435 nm is observed in the films. It is obvious from the figure that the intensity of photoluminescence increases considerably when the treatment temperature is 400 °C and above; it reaches its maximum at 500 °C and decreases drastically at 600 °C. Figure 7b shows the photoluminescent spectra of malonic alumina films heat treated at different temperatures under a 330-nm excitation. As the temperature rises from 100 to 200 °C, the intensity of photoluminescence increases. For films heat treated at 300 and 400 °C, the intensity of photoluminescence drastically decreases, and their emission spectra almost resemble the spectrum of the as-grown film. Comparing these results with spectra obtained for the oxalic acid alumina films heat treated at the same temperatures, we assume that quenching of luminescence may be accounted for the presence of excessive electrons on the carbon atom in the methylene group. We should point out that this effect for malonic acid alumina films is observed only above a certain treatment temperature. It is evident from Fig. 7b that the intensity of photoluminescence for films heat treated at 500 °C increases again, reaches its maximum, and then drops after 600 °C. We explain this drop, similarly as in case of oxalic

acid alumina films [28], by thermal splitting of malonic acid species (as presented in Eq. 1) with  $\text{CO}_2$  emission.

## Conclusions

The following conclusions can be drawn from this study:

1. The heat treatment of malonic acid alumina films at temperatures from 250 up to 350 °C leads to considerable changes in the shape of voltammograms recorded during re-anodizing in tetra-borate solution under potential sweep conditions. We suggest that these changes are related to the loss of two hydrogen atoms from methylene group ( $\text{CH}_2$ ) of malonic acid species incorporated within the alumina barrier layer. These changes may be accounted for a negative charge formed on the carbon atom due to joining of two electrons of hydrogen atoms. As a result, such carbon atom will lose electrons under high electric field and will further behave as an electronic trap joining migrating electrons. These sites ensure an increase in the number of pathways for easy electron migration in anodic films, and one can observe an increase in the value of current jump at the initial stage of re-anodizing.
2.  $j_a$  vs.  $\varphi$  plots for oxalic acid alumina films heat treated at temperatures from 200 up to 450 °C behave in the same way during re-anodizing. Furthermore, no structural defects responsible for rising electron current are observed as a result of splitting of oxalic acid species at 400 and 450 °C.
3. The malonic acid species incorporated into the alumina barrier layer are likely to lose hydrogen atoms from methylene groups ( $\text{CH}_2$ ) under extremely high electric field.

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