

Effect of the Anodization Parameters on the Volume Expansion of Anodized Aluminum Films

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The effect of anodization parameters, e.g. anodizing voltage, anodizing current, duration time, electrolyte temperature, electrolyte type and concentration, on the volume expansion of anodized Al, Al-1wt%Si and Al-1%Cu thin films have been studied. The volume expansion factor of anodic porous alumina is found to vary from 1.32 to 2.08, depending on the anodizing voltage, anodizing current density and electrolyte type. The electrolyte temperature and impurity type have slight effect on the volume expansion factor. The relation between the pore density of porous alumina and the anodizing voltage is found to follow the relation $N_p = 9.4 \times 10^{10} \exp(-0.042V)$. In addition, the current efficiency during the anodization was determined to be about 83%.

Keywords: Anodic aluminum oxide, volume expansion factor, pore density, the current efficiency

1. INTRODUCTION

Anodic aluminum oxide (AAO) was reported at first time more than fifty years ago. Since that it has attracted scientists and engineers attentions in many fields [1-3]. Two different types of AAO are exist: the nonporous barrier oxide and the porous oxide. Porous anodic alumina (PAA) is formed via an electrochemical process (anodization). The anodization of aluminum in acidic media results in a self-organization of hexagonal array of pores with an inter-pore distance controlled by the voltage. The porous structure provides a large effective surface area on a small footprint and can, amongst others, be used as templates for the fabrication of nanodots, nanowires and nanotubes[4,5]. To obtain perfectly straight pores, the anodization is typically done by a two-step process at low temperatures (< 5°C) [6,7]. This highly ordered pore configuration is achieved on bulk Al through a lengthy two-step

anodization producing membranes up to 200 μm thick with ordered domains up to several microns in lateral size. For the silicon integrated PAA films the aluminum thickness is limited due to the metal deposition process. To maximize the porous alumina thickness a one-step anodized process is needed, preferably at room temperature. In many cases, commercial aluminum foils are used of which the purity levels of it are not known or controlled [8-13].

The pore ordering has been attributed to the reaction of the mechanical stress that exists during the conversion of aluminum to alumina [14]. Various processes that occur during anodization of aluminum give rise to stress in both the alumina and the underlying substrate. Stress in the oxide film can lead to cracks and delamination, which affect the functional properties of alumina. Stress can occur due to volume change of thin film, thermal mismatch, vacancy incorporation, lattice mismatch, grain growth and other growth happens by creep mechanisms. Among these parameters, volume expansion of thin film during anodization strongly enhances the mechanical stress and affects the pore formation.

Gösele and co-workers showed that the ratio of overall film thickness to depth of metal consumed "volume expansion", is consistently close to 1.4 for ordered films grown in different baths [15]. They suggested a relationship between volume expansion and mechanical stress, and argued that PAA ordering is in part controlled by stress.

Vrublevsky et al. studied the volume expansion of aluminum during porous oxide formation at galvanostatic regime [16]. They have shown that the volume expansion of alumina is linearly dependent on the anodizing voltage for films formed near the room temperature in sulfuric acid. According to their work the volume expansion was varied from 1.35 to 1.63 at anodizing voltages of 13 to 24 V. The volume expansion of alumina appeared to be influenced by incorporation of sulfate or oxalate anion from the electrolyte into the alumina film [17]. Recently, dependence of the volume expansion on the current density for PAA films formed on bulk and sputtering-deposited aluminum in sulfuric acid respectively at either 0 or 20°C was reported [18]. The volume expansion ratio of PAA as a function of anodic voltage (20-180V) in 5 wt % H_3PO_4 at low temperature 3°C was reported [19].

The aim of the present study is to investigate the effect of anodization parameter, e.g. anodizing voltage, anodizing current density, duration time, electrolyte temperature, doping Si or Cu, electrolyte type and concentration on the volume expansion of anodized aluminum thin films. The relation between the volume expansion factor and current efficiency during growth of anodic alumina formed in different acids is discussed.

2. EXPERIMENTAL

Thin films with three different compositions were prepared: pure aluminum (Al), aluminum doped with 1 wt. % copper (Al-1Cu) and 1 wt.% silicon (Al-1Si). Films of typically 2 and/or 2.6 μm were deposited by physical vapor deposition (PVD) on 200mm H-terminated (100) p-type silicon wafers ($\rho \approx 20 \Omega \text{ cm}$) already covered with 100nm of TiN or 3 μm SiO_2 . Anodization was performed for all experiments under potentiostatic and galvanostatic control in a two-electrode electrochemical cell. The electrolyte bath temperature was investigated over the range 0°C to 50°C. The temperature controlled by immersing the electrochemical cell in a water bath (Haake C10) integrated with a chiller

(Haake EK20) and a thermostat (Haake D1) to set the desired temperature within $T \pm 0.1$ °C. The exposed area of the aluminum surface to the anodization process, was held constant at 5cm^2 (circular). The as-deposited thin-film was used as the working electrode while the counter electrode was Ti sheet ($5 \times 3.5\text{cm}^2$). Three different electrolytes; sulfuric acid (1M), oxalic acid (0.3M) and (0.75M) phosphoric acid were used as the acidic media needed for the anodization process under voltage and current density ranges of 5V-90V and $5\text{-}70\text{ mA cm}^{-2}$, respectively. The potential and current was supplied by an AUTOLAB PGSTAT100, controlled by Gpes electrochemical software, using AUTOLAB voltage multiplier. After the anodization process, the samples were rinsed in de-ionized water and dried in nitrogen gas. The measurement of the step between the anodized part and non anodized part (Height) was carried out using a $\pm 5\text{nm}$ resolution DEKTAK service profiler equipped with a computer signal-processing. The structures of porous alumina were characterized using a scanning electron microscope (SEM) Model Philips XL30. ImageJ Java image processing software was used for quantitative analysis of pore size and pore density.

3. RESULTS AND DISCUSSIONS

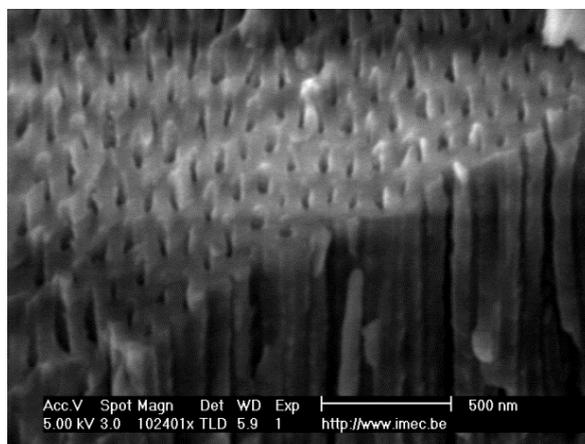


Figure 1. SEM cross section of porous alumina, the anodization of pure Al performed at RT in 0.3M oxalic acid at anodizing voltage 40V.

Figure 1 shows SEM cross section of porous alumina. This alumina film was performed by anodization of pure Al in 0.3M oxalic acid at anodizing voltage 40V at RT (22°C). The consumed charge to transform $2\mu\text{m}$ of aluminum to alumina by anodization is constant and is equal to 5.6C cm^{-2} for all Al anodization experiments.

Figure 2a and 2b show pore diameter d_p and the pore density N_p as a function of anodizing voltage, respectively determined from SEM image processing. The pores diameter exponentially increases while the pore density is exponentially decrease as the anodizing voltage increase in contradiction with the previously reported data [20]. Vico et al [20] reported that N_p was found inversely proportional to the cell voltage. The relationship between d_p or N_p with V can be deduced from the experimental finding of Figure 2a and 2b:

$$d_p = 14 \exp^{(0.02V)} \quad \dots (1)$$

$$N_p = 9.4 \times 10^{10} \exp^{(-0.042V)} \quad \dots (2)$$

Those two empirical relations are applicable for Al-1Si and Al-1Cu since there are no significant effects of doping with silicon or copper on pore diameter and pore density.

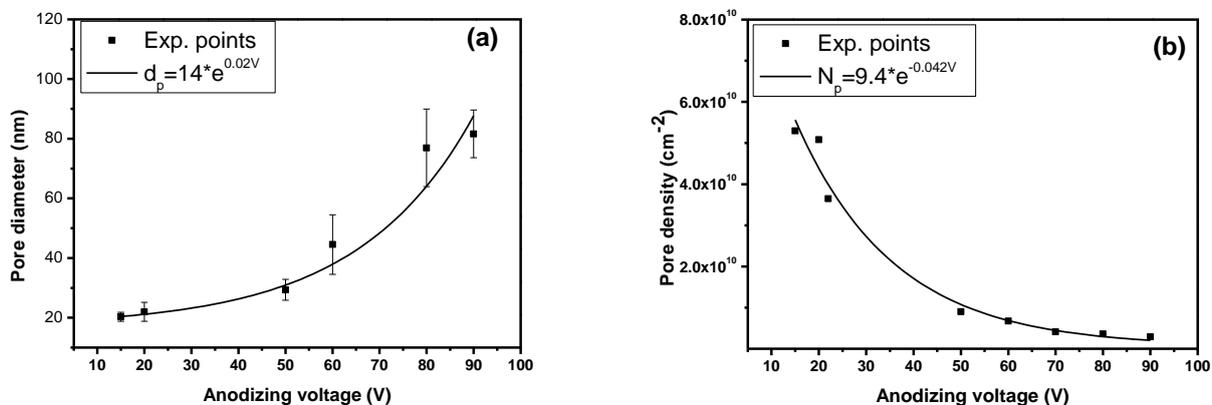


Figure 2. (a) Pore diameter versus anodizing voltage for alumina films on Si/SiO₂ after anodization in different electrolytes under potentiostatic control. Trend line, $d_p = 14 \exp^{(0.02V)}$. (b) Pore density versus anodizing voltage for alumina films on Si/SiO₂ after anodization in different electrolytes under potentiostatic control. Trend line: $N_p = 9.4 \times 10^{10} \exp^{(-0.042V)}$.

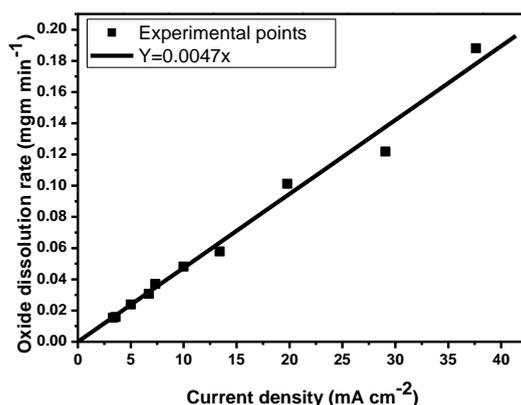


Figure 3. The rate (m t^{-1}) of Aluminum loss in mg min^{-1} versus current density for the 1 cm^2 of working electrode during anodization. The anodization was performed in sulfuric, oxalic and phosphoric acids at RT.

The loss rate of Al, the ratio of Al film thickness to the anodization time was used to determine the current efficiency (ϵ). Fig. 3 shows the rate of Al dissolved per 1 cm^2 of anode during the anodization versus current-density in sulfuric, oxalic and phosphoric acid at RT. The dissolved mass rate was measured in mg min^{-1} and the current density was obtained from the plateau region at the

transient curve during the anodization. The mass of dissolved alumina (m) in electrolyte during the anodization can be determined from equation (3):

$$m = N_p A d_p (L + \Delta L) \rho \quad \dots (3)$$

Here N_p pore density, A anodized area, d_p pore size, L aluminum thickness ($2\mu\text{m}$), ΔL the step height and ρ alumina density. The aluminum mass that was spent for oxide formation for duration time (t) can be calculated using the Faraday's law:

$$m t^{-1} = \epsilon k_0 i A \quad \dots (4)$$

where k_0 is the electrochemical equivalent and it is equal $0.0056 \text{ mgmA}^{-1}\text{min}^{-1}$ for Al [21]. Least-squares method for Figure 3 has given the following relation:

$$m t^{-1} = 0.0047 i \quad \dots (5)$$

Relation (5) is compared with equation (4) to find the current efficiency for electrode reaction and it is found to be close to 83%. It is also found that the current efficiency independent of the electrolyte type. This method is invalid to determine the current efficiency during anodization of Al-1Si and Al-1Cu due to the pore branching and interconnections [22,23].

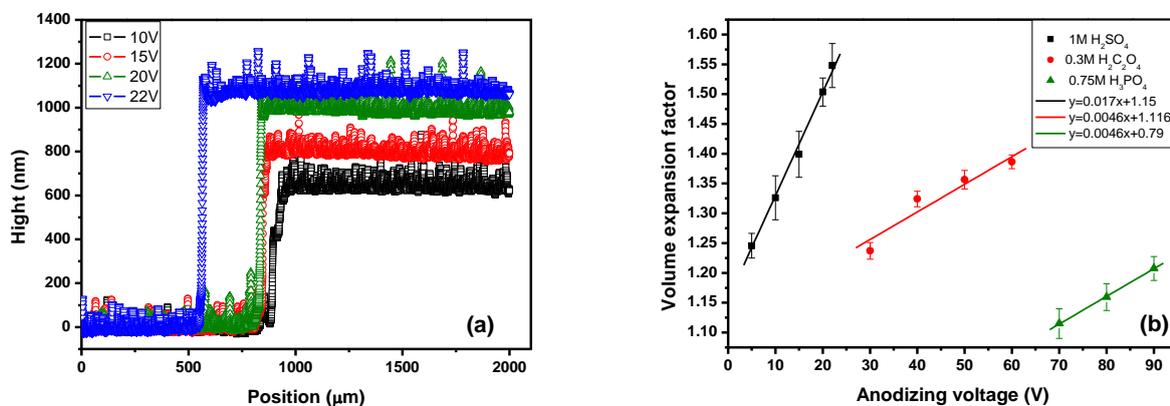


Figure 4. (a) The step height between the porous alumina surface and aluminum surface for anodized Al. The anodization of Al was performed in sulfuric acid at RT under potentiostatic control. (b) The volume expansion factor versus the anodizing voltage for anodized Al in sulfuric acid, oxalic acid and phosphoric acid at RT.

Fig. 4a shows the step height ΔL between aluminum surface and the porous alumina surface formed by anodization of pure aluminum in 1M sulfuric acid at different anodizing voltage at RT. It is found that the step height increases as the anodizing voltage increase for the same electrolyte, temperature and substrate. The volume expansion factor (k) is determined from the step height according to the following relation:

$$k = 1 + (\Delta L/L) \quad \dots (6)$$

Fig. 4b shows the volume expansion factor for pure Al samples versus anodizing voltage measured in 1M sulfuric, 0.3Moxalic acid and 0.75M phosphoric acid at RT. It is seen from Figs. 4b that, the volume expansion factor increases linearly as a function of the anodizing voltage for the same temperature, substrate, electrolyte and concentration. Longer anodization time and chemical etching

can explain the observed volume expansion factor with value lower than 1.4 than the expected 1.4 value [15]. In the case of partial transformation of aluminum into $Al(OH)_3$, a much larger volume expansion factor (>1.4) would be found. The volume expansion factor depends differently on the anodizing voltage in sulfuric acid, oxalic acid and phosphoric acid. The volume expansion factor of porous alumina films formed in sulfuric, oxalic and phosphoric acid changes from 1.24 to 1.56, 1.23 to 1.37 and 1.13 to 1.2 as the anodizing voltage changes from 10 to 22V, 30 to 60V and 70 to 90V, respectively. For similar anodization duration, the lowest expansion factors are indeed obtained for phosphoric acid and the highest for sulfuric acid. The alumina layer is chemically etched during the anodization process. The etching rate is fast in phosphoric acid and slow in sulfuric acid. The alumina formed in oxalic acid contain relatively low levels of oxalate incorporation (2.4 wt.% oxalate) comparing with the films formed in sulfuric acid (12-14 wt.% sulphate) [24]. Therefore, at the same anodizing voltage the volume expansion factor for sulfuric acid is greater than oxalic acid. The linear fit of the volume expansion factor of porous alumina dependence on the anodizing voltage is performed to give the following formula for 1M sulfuric acid, 0.3M oxalic acid and 0.75M Phosphoric acid respectively

$$k=0.017V+1.15 \quad \dots (7)$$

$$k=0.0046V+1.116 \quad \dots (8)$$

$$k=0.0046V+0.79 \quad \dots (9)$$

The proportional constant between k and V depends on the electrolyte type. It is larger for sulfuric acid than the oxalic and phosphoric acid.

Effect of Doping with Si and Cu on the Volume Expansion Factors:

Fig. 5a shows the volume expansion factor for Al-1Si samples versus anodizing voltage curves measured in 1M sulfuric, 0.3M oxalic acid and 0.75M phosphoric acid at RT.

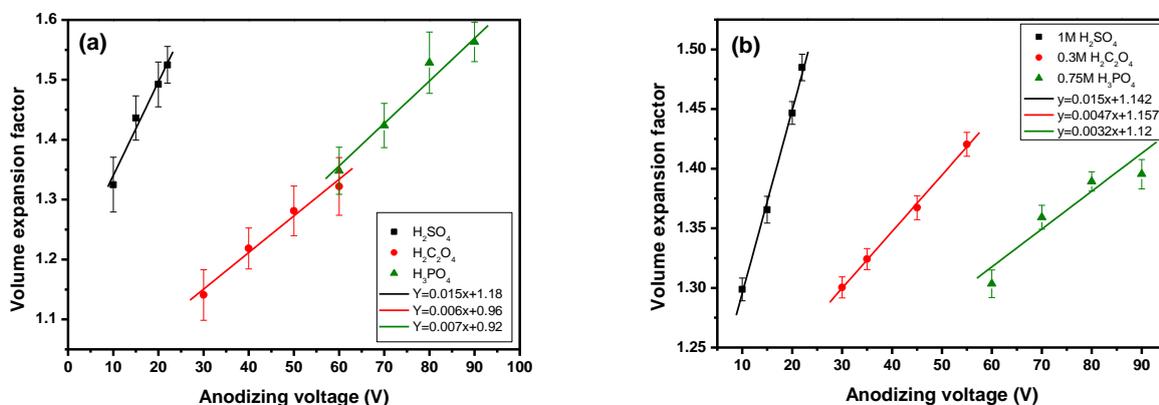


Figure 5.(a) The volume expansion factor versus the anodizing voltage for anodized Al-1Si in sulfuric acid, oxalic acid and phosphoric acid at RT. (b) The volume expansion factor versus the anodizing voltage for anodized Al-1Cu in sulfuric acid, oxalic acid and phosphoric acid at RT.

It is seen from Figs. 5a that, the volume expansion factor increases linearly as a function of the anodizing voltage at the same temperature, substrate, electrolyte and concentration. The volume expansion factor of porous alumina films formed in sulfuric, oxalic and phosphoric acid changes from 1.33 to 1.54, 1.14 to 1.32 and 1.35 to 1.56 as the anodizing voltage changes from 10 to 22V, 30 to 60V and 60 to 90V, respectively. The linear fit of volume expansion factor of porous alumina dependence on the anodizing voltage is performed to give the following formula for 1M sulfuric acid, 0.3M oxalic acid and 0.75M Phosphoric acid respectively

$$k=0.015V+1.18 \quad \dots (10)$$

$$k=0.006V+0.96 \quad \dots (11)$$

$$k=0.007V+0.92 \quad \dots (12)$$

The proportional constant between k and V depends on the electrolyte type. It is larger for sulfuric acid than the oxalic and phosphoric acid. The average intercept is close to one as at anodizing voltage goes to zero for all cases. The proportionality constant between k and V for Al-1Si and pure Al anodized in sulfuric acid is the same while it has a greater value than samples anodized in oxalic or phosphoric acid.

Fig. 5b shows the volume expansion factor for Al-1Cu samples versus anodizing voltage measured in 1M sulfuric, 0.3Moxalic acid and 0.75M phosphoric acid at RT.

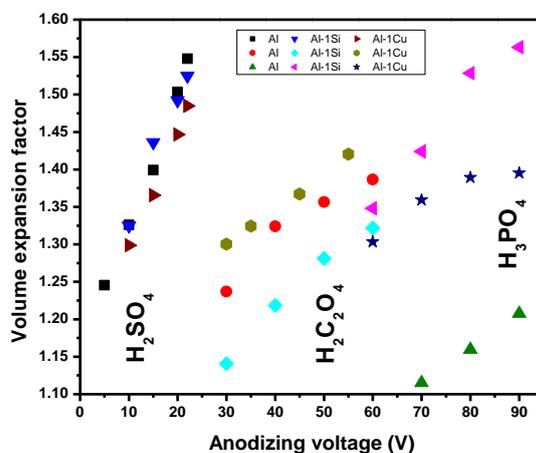


Figure 6. The volume expansion factor versus current density for anodized Al in sulfuric acid, oxalic acid and phosphoric acid at RT.

It is seen from Figs. 5a that, the volume expansion factor increases linearly as a function of the anodizing voltage at the same temperature, substrate, electrolyte and concentration. The volume expansion factor of porous alumina films formed in sulfuric, oxalic and phosphoric acid changes from 1.3 to 1.48, 1.3to 1.42 and 1.31 to 1.39 as the anodizing voltage changes from 10 to 22V, 30 to 60V and 70 to 90V, respectively. The linear fit of volume expansion factor of porous alumina dependence on the anodizing voltage is performed to give the following formula for 1M sulfuric acid, 0.3M oxalic acid and 0.75M Phosphoric acid respectively

$$k=0.015V+1.142 \quad \dots (13)$$

$$k=0.0047V+1.157 \quad \dots (14)$$

$$k=0.0032V+1.12 \quad \dots (15)$$

The proportional constant between k and V depends on the electrolyte type. It is also larger for sulfuric acid than the oxalic and phosphoric acid.

The comparison of the relation between volume expansion factor and the anodizing voltage for Al, Al-1Si and Al-1Cu is summarized at Figure 6. No significant effect is seen in doping with silicon or copper on the volume expansion for samples anodized in sulfuric acid. For porous alumina samples performed in oxalic or phosphoric acid there is good agreement with plateau current observed in the transient curve during the anodization [22,23].

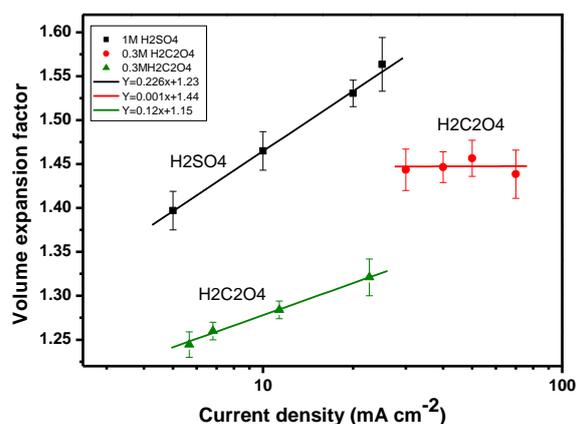


Figure 7. The volume expansion factor versus current density for anodized Al in sulfuric acid and oxalic acid at RT.

Fig. 7 shows the volume expansion factor for pure Al samples versus anodizing current density curves measured in 1M sulfuric and 0.3M oxalic acid at RT for the same substrate, electrolyte and concentration. It is seen from Figs. 7, the volume expansion factor increases with the anodizing current density till 22 mA cm⁻² to be constant after 30 mA cm⁻². The volume expansion factors of porous alumina films formed in sulfuric and oxalic acids change from 1.4 to 1.57 and 1.25 to 1.32 as the anodizing current density change from 5 to 27 and 5.8 to 25 mA cm⁻² respectively. The volume expansion factor of porous alumina films formed in oxalic acid becomes constant at 1.44 for anodizing current density range from 30 to 70 mA cm⁻². The linear fit of volume expansion factor of porous alumina dependence on the anodizing current is performed to give the following formula for 1M sulfuric acid, 0.3M oxalic acid ($i < 22 \text{ mA cm}^{-2}$) and 0.3M oxalic acid ($i > 30 \text{ mA cm}^{-2}$) respectively;

$$k=0.226\ln(i)+1.23 \quad \dots (16)$$

$$k=0.12\ln(i)+1.15 \quad \dots (17)$$

$$k=0.001\ln(i)+1.44 \quad \dots (18)$$

The proportional constant depends on electrolyte type. The volume expansion factor remains constant for samples anodized in oxalic acid at current density greater than 30 mA cm⁻². The average intercept is close to 1.27. The constant volume expansion factor for samples anodized at current density greater than 30 mA cm⁻² is attributed to the samples burns and delimitation, Figure 9c. The anodization at high current density leads to void formation at the metal/oxide interface. In that case,

there is a high possibility for the PAA template to lift-off from the silicon oxide substrate. This is caused by the added tensile pressure of H_2 gas at the PAA/ SiO_2 interface on top of the pre-existing stress the sample experiences due to the volume expansion during the anodization of aluminum to form alumina.

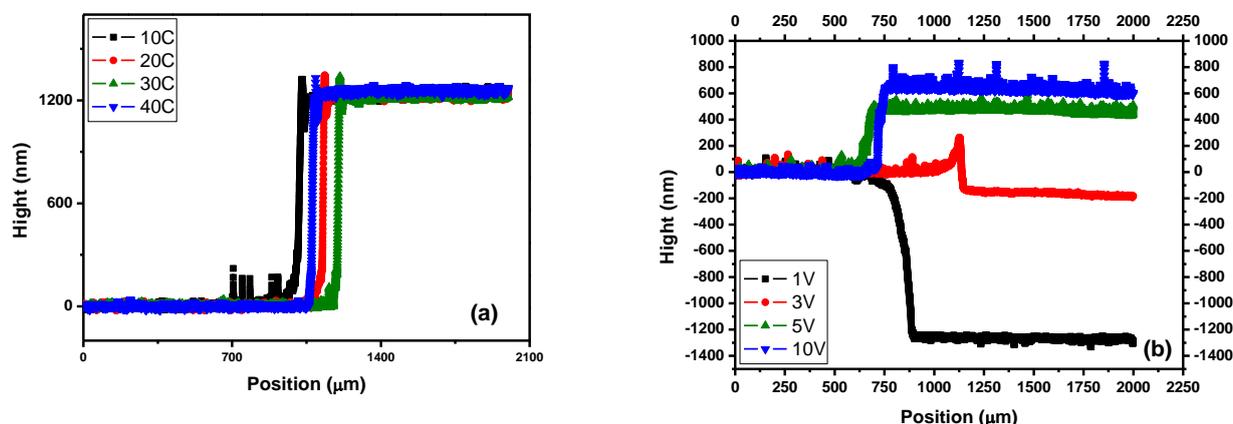


Figure 8. (a) The step height between the porous alumina surface and aluminum surface for anodized Al-1Cu. The anodization of Al-1Cu was performed in 1M sulfuric acid at 22V and different electrolyte temperature. (b) The step height between the porous alumina surface and aluminum surface for anodized Al. The anodization of Al was performed in sulfuric acid at low anodizing voltage at RT and under potentiostatic control.

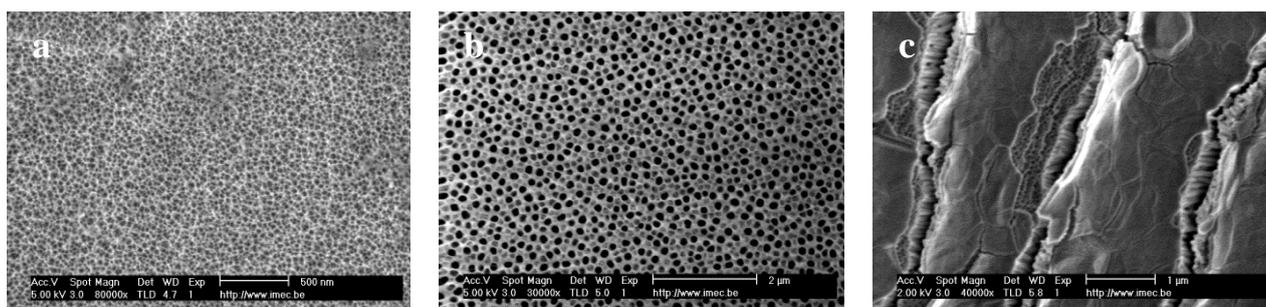


Figure 9. Top view of porous alumina for (a) the anodization of pure Al performed at RT in 1M sulfuric acid at anodizing voltage 1V, (b) the anodization of Al-1Cu performed at RT in 0.3M oxalic acid at anodizing voltage 80V and (c) the anodization of pure Al performed at RT in 1M sulfuric acid at anodizing current density 50mA cm^{-2} .

Figure 8a shows the expansion of anodized Al-1Cu in 1M sulfuric acid at 22V at different electrolyte temperature (10°C to 40°C). The expansion is slightly increases as the electrolyte temperature increase. The similarity of expansion at different temperature might be attributed to: (1) the increase of ion migration and thus lower duration time, and (2) increases of the chemical etching as electrolyte temperature increases.

For the anodization at low voltage (<5V), the thickness of alumina becomes lower than the original thickness of aluminum, Figure 8b. This observation is attributed to the long anodization time which reached to more than 3 hours, lower ion migration and low anodization rate.

The anodization at low voltage leads to un-regular pores with small thickness, figure 9a. To avoid the alumina dissolution during the anodization at low voltage and burning at high current density, anodization at intermediate voltage is required to form a regular pore as observed in Figure 9b.

4. CONCLUSIONS

During the potentiostatic anodization, the pore diameter exponentially increases while the pore density exponentially decreases, as the anodizing voltage increase, in contradiction with the previously reported data. As the current density increases in the range of 1-22mA cm⁻² the volume expansion is exponentially increased while it remains constant at higher current density (>30mA cm⁻²). No significant effect of electrolyte temperature, in range of 0-50°C, on the volume expansion factor. The effect of impurity on the volume expansion factor can be neglected. The electrolyte type strongly affects the volume expansion factor. The volume expansion factor of anodic porous alumina varied from 1.32 to 2.08 and the average current efficiency 83%.

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