Novel pre-oxidation patterning on thin aluminum film generating ordered nanopores through anodization

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ABSTRACT

Anodic Aluminum Oxide (AAO) is widely employed as a template for fabrication of nanowires and nanotubes due to its ability to generate self organized (SO), well ordered pore structures. We have developed a new aluminum pre-patterning technique to create well ordered nanopore arrays on thin films deposited on silicon substrates. We form patterns of thicker oxide on the surface via local oxidation process using a conducting Atomic Force Microscope (AFM) tip working in contact mode. Pores are forced to nucleate between the pre-oxidized regions during the anodization process. The relation between applied voltage and ordered interpore distance has been found to be linear for these supported thin films. However, the pore spacing is highly reduced compared to free standing foils. A new empiric law has been confirmed for a wide range of voltages, solution concentrations and different electrolytes, including oxalic and phosphoric acid. Our results show that pre-oxidation patterning is an alternative technique to achieve an ordered nanoporous template through the anodization process.

INTRODUCTION

Porous anodic alumina (PAA) has long been considered a promising material for templated growth of nanostructured materials for application in electronics, magnetics and optics[1-3], as well as mask for pattern transfer through wet and dry etching[4]. Since Masuda *et al.*[5] reported the formation of highly ordered porous layers of aluminum oxide with a hexagonal configuration, an increasing emphasis has been put on PAA capabilities to give easy access to a self-organized ordered array of hexagonal pores with high aspect ratio and tunable pore size, with exceptional thermal stability over a wide range of temperature.

Anodization is an electric field-enhanced process during which a pore develops in a sequence of three steps: Random nucleation on the surface; self organization, in which pores rearrange under the surface to achieve a close packed, ordered configuration; and steady state pore growth. While self-ordering in PAA has been studied for more than 50 years, a comprehensive theoretical model explaining pore formation yet to be developed. Most proposed models examine the self organization process and the steady state pore growth. In 1998, Jessensky *et al.*[6] proposed that self organization was driven by mechanical stress at the metal/oxide interface due to the volume expansion of the aluminium during oxidation. This induced stress creates an upward flow of the oxide from the pore bottom, driving pore rearrangement during anodization. Several years later, Garcia-Vergara *et al.*[7] carried out a study employing a tungsten tracer layer which became incorporated into the anodic film from the

aluminium substrate. Distortions of the tungsten layer on entry into the film and retention of tungsten species in the film are compatible with porosity arising mainly from flow of anodic oxide beneath the pore base towards the cell walls. A recent theoretical model proposed by Houser *et al.* [8] investigated the role of viscous flow of oxide in the growth mechanism of porous anodic films. Their calculations suggest that the viscous flow originates from high local compressive stresses close to the pore base. The location of this stress excludes explanations for flow based on the volume increase on conversion of metal to oxide. They speculate that this flow is due to the competition of strong anion adsorption with deposition of oxygen.

Compared to other aspects of PAA formation, pore nucleation is less understood. O'Sullivan *et al.* [9] proposed that, since anodization is a field assisted process, a pore will nucleate where the local electric field is stronger. This condition is achieved when the metal/oxide interface at the Al surface is angled away from the horizontal, and the electric field is concentrated due to a change in local surface morphology. This condition is apparently exploited in all reported pre-patterning techniques used to induce pore ordering. To accomplish this, the surface morphology is altered by creating physical pits that act as seeding points for the pore development. High resolution processes to do this range from the mechanical imprinting [10] to e-beam and ion beam lithography [11-12]. Alternatively, it seems likely that a small region in which the native oxide layer is thinner respect to the surrounding area could create a strong electric field concentration. This has been recently demonstrated for the first time by our group [13]. As the native oxide layer is very thin and inherently uneven, proving this assertion is challenging. Previously, we have modified the aluminum surface chemistry creating patterns with different oxide thickness. A grid of patterned oxide was created using a local oxidation process with a conductive atomic force microscope (AFM) cantilever and the pore nucleation was studied in these pre-oxidized regions after anodization. These results showed that these pre-oxidized patterns have the capability to control pores nucleation and induce pore ordering during the anodization process. This is suitable for multilayer technology in which the imprinting process can damage the sample layers due to the high external pressure exerted on the surface.

The study presented here extends these results [13] to diluted oxalic acid and phosphoric acid solutions as electrolytes and with different applied voltages in the range 40-120V.

EXPERIMENT

Substrates were prepared by depositing a 200 nm aluminum (Kurt J. Lescker 99.999%) films via e-beam evaporation onto 6 inch p-type (100)-oriented silicon wafers (Si-Mat Silicon Materials). A 10 nm titanium (Kurt J. Lescker 99.995%) layer was evaporated as an adhesion layer between the Al and Si substrate. The Al films were pre-patterned using a proximal electrical contact process to form grids of oxide lines on the surface. The surface between oxide lines becomes the seeding point for pore nucleation. The pre-oxidation patterning was carried out by an Asylum Research MFP-3D atomic force microscope (AFM) in contact mode under ambient air conditions with platinum/iridium coated electro-levers (model AC240s) purchased from Asylum Research. A bias of -10 V was applied to the tip and the scan velocity was 80 nm/s. The patterned substrates were anodized in a custom-built anodization cell. A platinum grid was used as the counter electrode placed at a fixed distance of 5 cm from the sample. The solution was constantly stirred during the anodization process. After pore formation, the samples were analyzed using a ZEISS Ultra scanning electron microscope (SEM), an FEI Strata 240Dualbeam system and an FEI transmission electron microscope (TEM) Titan.

Figure 1a shows an AFM image of the 200 nm Al surface deposited on a Si substrate after the pre-oxidation patterning. The pattern created on the surface is a grid of 100 nm pitch. The oxide lines are easily visible on the surface and, as shown in the inset, the patterned oxide protrudes from the surface by about 3 nm. Figure 1b shows a TEM image of an FIB-prepared sample cross-section taken at transverse angle to the patterned oxide lines of a similarly prepared sample. In the image, various sample layers are visible: Moving up from the bottom, we start with a silicon oxide layer present at the surface of the silicon wafer, followed by the 10 nm titanium adhesion layer (dark line.) The full Al film can be seen above this in lighter grey. At the top of the Al film, the patterned oxide is visible as a layer with thickness periodically changing, the mid-point of the oxide lines shown with black arrows. The two insets in the upper part of the figure are a magnifications of the patterned region (left) showing two lines of oxide and a magnification of the Al surface without pre-oxidized pattern (right). The maximum thickness of the patterned oxide is 13 nm while the minimum (native oxide) thickness between two lines is about 3-4 nm.

Figure 1. a) AFM image of a pre-patterned oxide grid on a 200nm aluminum film. The pattern is easily visible on the surface. A line profile shown in inset corresponds to the region indicated by the red line in the main image. It shows the oxide patterns protrude from the surface by about 3nm. b) TEM cross section image of the surface below a pre-patterned oxide grid. The arrows show the mid-point of the oxide lines. Insets at the top of the figure show a additional detail of the oxide lines (left) and an area with only the native oxide present (right). Scale bars indicate 20 nm in the insets and 50 nm in the main picture.

Samples were patterned with square grids of different pitch and pore nucleation positions inside the patterned area were studied. Inside the grid, square areas surrounded by four oxide lines are present and, for our study, they are considered as the active surface for pore nucleation. Each of these regions is considered as an *available position* for the nucleation of one pore. The patterns so created had 80, 100, 120, 150, 170, 200 and 220 nm pitch.

After the pre-oxidation patterning, the samples were anodized with two different electrolytes to create the porous media. A 0.03 M solution of oxalic acid (Fisher Scientific) was employed and the anodization process was carried out at three different potentials of 40, 80 and 120 V at room temperature. A 0.2 M solution of phosphoric acid (Fisher Scientific) was used for

anodization at 80V at room temperature and with concentration 10%wt for an applied voltage of 120V at 4°C.

DISCUSSION

Pre-oxidation patterning

A well ordered pore array can be obtained by a two step anodization process [5] or by a pre-textured pattern [10], as discussed above. The self organization in the two step process is achievable only in a narrow window of voltages and temperatures for a given choice of electrolyte. For example, the best self-arrangement with sulfuric acid is obtained with 0.3 M solution and applied voltage of 25 V. For 0.3 M oxalic acid solutions, there is formation of well ordered hexagonal arrays with an applied voltage of 40 V and for 10%wt phosphoric acid solutions, the self-ordering is achieved at an applied 160 V [14]. Beyond these specific self-organization windows, it is possible to induce pore ordering by pre-patterning the surface with an array of pits that act as nucleation points for the nanochannel development. Matching the patterned pitch length with the correct applied voltage is crucial in this process [11], otherwise pore will nucleate and develop outside the textured pattern. Recently, Lee et al. [15] showed that new self-ordering regimes could be established through the so called *hard anodization*. Well ordered porous arrays with pitches varying between 220 and 300 nm can be obtained anodizing aluminum foils with oxalic acid solution and applied voltages between 120 and 150 V.

The study presented in this paper starts from the assumption that flat regions with a thinner oxide layer with respect to the surrounding area can create a strong electric field concentration enhancing the anodization process. The TEM cross section in Figure 1b shows that the thickness of the patterned oxide is 13 nm while the native oxide is about 3-4 nm. As a consequence, the oxide patterning process adds only about 10 nm which is nevertheless sufficient to influence the pore nucleation location during the anodization process.

To establish this, we introduced [13] a *fill parameter*, ξ , to evaluate the matching between the imposed pattern and the pore pattern formed during anodization. ξ is defined as the ratio between the number of pores present in the patterned area, n_p , and the number of available positions, n_a , $\xi = n_p / n_a$. The available position in a grid is a square region surrounded by four oxide lines. Perfect matching between patterned nucleation points and number of pores formed returns a fill parameter of 1; ξ is less than 1 if the available positions are not filled completely. In this case we talk about *under-filling* of the patterned region. Under-filling is present when the patterned pitch is shorter than the corresponding interpore random distance at the imposed applied voltage. Finally, ξ is higher than 1 when more than one pore is present in an available position where we refer to *over-filling* of the patterned region. Over-filling is achieved when the patterned pitch length is longer than the random interpore distance. This parameter together with the FFT analysis of SEM images taken on the patterned regions forms an indicator of the effectiveness of pre-patterning.

Figure 2 shows an example of anodized aluminum surfaces with oxalic acid 0.03 M at 80 V. Figure 2a depicts a non-patterned area where random pore nucleation is visible and highlighted by a structureless FFT ring (inset). Figure 2b shows the pore nucleation in a pre-patterned region within a grid of 80 nm pitch. This is an example of under-filling condition: Pores do not nucleate in all available positions in the grid, leaving skipped positions. The discrete rectangular patterns

in the FFT inset demonstrate that although this array is not perfectly filled, an order is maintained in the patterned region. Pores do not nucleate randomly anywhere in the region but only inside the defined positions surrounded by the pre-oxidized lines. Figure 2c shows a perfect square array of pores formed on a pre-oxidized grid with 120 nm pitch. The perfect matching is highlighted by the rectangular pattern present in the FFT inset. The fill parameter for this pattern is $\xi=1$. Figure 2d provides an example of the over-filling condition with a wider pre-oxidized pattern of 200 nm pitch. Inside each available position more than one pore has nucleated. The fill parameter has a value higher than 1. Here, pore nucleation sites remain confined inside the patterned oxide lines and most of them are located in the interface region between the aluminum and the oxide lines. The electric field in the Al/oxide interface is enhanced by the difference in electrical conductivity between the two materials. Again, a certain order is imposed by the oxide lines which is visible in the FFT image inset.

Figure 2. 200 nm aluminum film deposited on silicon anodized with oxalic acid 0.003M at constant voltage of 80 V at room temperature. a) Random pore nucleation in a non-patterned region. b) *under-filling*. Pre-oxidized grid with 80nm pitch. Pores do not nucleate in all the available positions in the grid but some positions are skipped. c) Perfect matching between pre-oxidized grid with 120nm pitch and pore nucleation. A perfect square array of pores is shown. d) *over-filling*. Pre-patterned oxide grid with 200nm pitch. Inside each available position more than one pore has nucleated. The space inside each region surrounded by oxide line leaves enough for the nucleation of more than one pore. The insets in each picture show the FFT of the pattern. The black bars indicate 200 nm.

Empirical law for diluted oxalic acid

Data obtained by anodization with oxalic acid 0.03 M solution at different voltages are summarized in Figure 3. The random interpore distance measured on thin 200 nm Al films evaporated on silicon substrates are 80 nm for applied voltage of 40 V, 120 nm for voltage of 80 V and finally 170 nm for 120 V. These values are indicated as open circles in Figure 3a. Figure 3a shows also that the *patterned grid pitch vs. applied voltage* space is divided into three different regions. These regions are qualitatively similar to our previous results [13] for anodization carried out with oxalic acid 0.3M at different voltages. It is possible to define a region (purple) of under-filling condition, $\xi < 1$, for grid pitches shorter than 150 nm for applied voltage of 120 V, shorter than 100 nm for voltage of 80 V and shorter than 80 nm for 40 V. The shortest pitch length achieved in this study is 80 nm, so we presently have limited information for shorter pitch lengths at 40 V. A region of perfect matching, $\xi = 1$, with very well ordered pore arrays, is defined around a patterned pitch length comparable with the random interpore distance. The central region (red) in Figure 3a shows that a perfect square pore array is obtained with pitch length of 80 nm at 40 V, 100 and 120 nm at 80 V and 150 and 170 nm at 120 V. Finally, the upper region (grey) defines the over-filling regime, $\xi > 1$. This is achieved with pre-oxidized patterns with pitch longer than 100 nm at 40 V, 150 nm at 80 V and 200 nm at 120 V.

By interpolating the data showing perfect filling, it is possible to define an empirical law relating the external applied voltage with the achieved interpore distance. Using a linear fit with data inside the red region we obtain a linear relation described by $D_{int} = 1.04(nm/V) * V + 33nm$, where D_{int} is the interpore distance and V the external applied voltage. The linear coefficient defined here for thin supported films is lower than the coefficient described for aluminum foils. It is well known that the coefficient relating interpore distance and applied voltage for foils anodized by oxalic acid is 2.5 nm/V. Figure 2b compares the empirical law for foils and thin films. As can be seen, the reduced slope for thin films means that at the same applied voltage the achieved interpore distance is lower for thin films than for foils.

Figure 3. a) Interpore distance (D_{int}) plotted against applied voltage for the anodization process of a 200 nm Al film deposited on silicon. Data refer to anodization with oxalic acid solution 0.03M. The D_{int} vs. V space is divided in three distinct regions: the bottom region

(purple) represents patterned pitches for which under-filling regime, $\xi < 1$, is present; the central area (red) described a regime of perfect matching between imposed patterning and pore order. In this region well ordered square templates are achieved. Upper region (grey) describes patterned pitches for which over-filling regime, $\xi > 1$, is experienced. b) Comparison between empirical law relating interpore distance with applied voltage for Al foils and Al thin films supported on silicon substrates. The linear relation for Al thin films shows a lower slope than for Al foils. At the same applied voltage the interpore distance obtained is shorter for Al thin films.

Fill parameter

Figure 4a shows the fill parameter evaluated at different pre-patterned grid pitches during anodization with 0.03 M oxalic acid at three different voltages. Starting from a 80 nm pitch, ξ begins from values less than 1, and increases with pitch. For 80 and 120 V potentials, a plateau is reached when ξ reaches a value of 1, indicating the ability of the pre-patterning to influence the random interpore distance. This plateau corresponds to the single pore filling region of Figure 3a. After this plateau, the fill parameter increases again with increasing pitch length. For 40 V anodization, ξ increases monotonically with pitch because the random interpore distance is already 80nm at this voltage, matching the smallest pitch of our grids. For all cases, increasing the pitch length leads to over-filling. At an applied voltage of 80 V, the ξ plateau lies between values of 100 and 120 nm in pitch. For larger pitch, the fill parameter raises rapidly to values of 1.4 at 150 nm and 2.7 at 200 nm. The latter value means that inside each available position in the grid there is an average of about 3 pores. The plateau for 120 V is between 150 and 170 nm. For 200 nm pitch the fill parameter does increase, but not as rapidly as the 80 V case.

Comparing the results shown in this paper with data published on anodization of 200nm Al film supported on silicon substrates using oxalic acid at concentration of 0.3M[13], it is possible to observe a qualitative agreement in the data trend. Data at 80 V are in perfect agreement between 0.03M and 0.3M solution, while at 40V there is a general shift of the data points on the left side. The plateau was found to be between 80 and 100 nm with more concentrated solution. On the other hand, at 120 V the data for diluted solution are shifted on the right side. The plateau for 0.3M solution was found between 120 and 150 nm.

Figure 4. a) Fill parameter ξ vs. patterned pitch length for anodization carried out with oxalic acid solution 0.03M. Red squares represent data at applied voltage of 40V, green circles 80V, and blue diamonds 120V. b) Fill parameter, ξ , plotted against patterned pitch length for samples anodized with phosphoric acid solution. Purple squares refer to samples anodized with 0.3 M H_3PO_4 at 80V while green circles to anodization with 10%wt H_3PO_4 solution and applied voltage of 120V. Data with $\xi=1$ are highlighted.

Figure 4b shows ξ vs. pitch data obtained by anodization with phosphoric acid of pre-patterned 200nm Al films evaporated on silicon. The general data trend follows the behavior found for oxalic acid. Data at 80 V refer to phosphoric acid solution with concentration 0.2 M and room anodization temperature. The random interpore distance at this condition is $140 \pm 10\text{nm}$. Ordered square arrays of pores have been achieved with pre-oxidized patterns of 150 and 170 nm. Data at 120 V refer to a 10%wt phosphoric acid solution and anodization temperature of 4°C . The random interpore distance was $200 \pm 10\text{nm}$. Well-ordered square arrays were obtained with pre-oxidized pitch of 170 and 200 nm length.

Results discussion

We have extended our previous results [13] to different electrolyte with different concentrations and for different applied voltages. Square arrays of ordered pores have been created during anodization with 0.03M oxalic acid at 40, 80 and 120 V and with phosphoric acid solution at 80 and 120 V. The pre-oxidation process shows to be a valid patterning technique to drive pore ordering. We would like to stress here that the *active* oxide layer inducing pore nucleation is 10nm thick. This result suggests that the influence of the native oxide on pore nucleation mechanism on flat surfaces is a key point.

Our results on oxalic acid differ with that of Li *et al.*[11] for thick, free-standing Al foils. In that work, formation of perfect hexagonal array with interpore distance of 200 nm was shown, as formed on Al foils pre-patterned with electron beam lithography and anodized with oxalic acid 0.03M at 85V. Interpore distance of about 350nm for anodized aluminum foils with phosphoric acid solution 10%wt at 120V were reported by Li *et al.*[14]. Pores formed during anodization with phosphoric acid of thin supported aluminum films show a shorter interpore distance than aluminum foils anodized with the same experimental parameters. This behavior is in perfect agreement with our previous results[13] on thin supported Al film anodized with oxalic acid. Grown thin films on silicon substrates showed a reduced interpore distance respect to the correspondent foils. We suggested this reduction is due to the stress induced on the film by the silicon substrate. As shown in Figure 2a, perfect ordered arrays are not obtained only for pre-patterned pitch length equal to the random interpore spacing. Ordered pore structures are also achieved for pitch length 20nm shorter. This is emphasized by the presence of the plateau in plots shown in Figure 4. Along the plateau the pore spacing can be modify without changing the anodization conditions.

Our new empirical law relating applied voltage and interpore distance for dilute 0.03 M oxalic acid anodization shows good agreement with our results for concentrated 0.3 M oxalic solution. The linear coefficient for the dilute solution is 1.04 nm/V while it is 0.6nm/V for the concentrated solution. While the coefficients differ from each other by about 40%, they are

factors lower than the empirical linear coefficient for anodization of Al foils with oxalic acid of 2.5 nm/V. We suggest the difference in the linear coefficient is due to the reduction in the interpore distance for thin Al films supported on silicon substrate induced by stress imposed by the substrate. A reduction in the random interpore distance has been found also for anodization carried out with phosphoric acid solution. This effect seems to not be influenced by the electrolyte or the applied voltage. It is related to the substrate characteristics.

CONCLUSIONS

In summary, we have studied pore nucleation on thin aluminum films deposited on silicon substrates under anodization with oxalic and phosphoric acid at various voltages. The Al surface was pre-patterned with a novel technique developed by our group. Grids of oxide lines were created on the surface surrounding small areas with thin native oxide. The pre-oxidation patterning is a valid technique to induce pore ordering in a wide range of applied voltages and electrolyte used. These results are in good agreement with and extend our previous study carried out on anodization of thin supported Al film with 0.3M oxalic acid [13]. It has been demonstrated that an oxide layer of 10nm thickness can drive pore nucleation during anodization of aluminum. This general result is a starting point for the understanding of pore nucleation on flat substrates.

Random interpore distance for anodization with phosphoric acid solutions of supported thin Al films is lower than the published for Al foils. These results suggest that the lower interpore distance shown after anodization of supported films is not related to the anodization conditions but is due to some specific characteristic of the substrate. We believe that the silicon substrate induces residual mechanical stress in the thin film constraining the interpore distance. The plateau present in the ξ vs. pitch data plot highlights the ability to modify the pore spacing maintaining fixed the experimental conditions.

The empirical law relating interpore distance and applied voltage for diluted oxalic acid has been found to have a linear coefficient lower than that of Al foils. This means that for the same experimental conditions, the interpore distance for a thin Al film deposited on silicon substrates is shorter than for Al foils. The same behavior has been found previously anodizing the same substrates with more concentrated oxalic solution [13].

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