Mechanism of guided self-organization producing quasi-monodomain porous alumina

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Abstract

It has been recently demonstrated [J. Choi, K. Nielsch, M. Reiche, R.B. Wehrspohn, U. Gösele, J. Vac. Sci. Technol. B 21 (2003) 763] that quasi-monodomain porous alumina with 300 nm interpore distance can be obtained by means of a 500 nm periodic master stamp applying the guided self-organization process. In this article, a theory based on suppression of the field-enhanced oxide dissolution at a wedge is suggested to explain the preparation of highly-ordered porous alumina with an interpore distance having 0.6 times the lattice constant of the master stamp. In addition, the occurrence of triangular pores, which is observed during the growth of pores by guided self-organization, can be explained and will be discussed in detail.

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1. Introduction

Since the discovery of self-ordered growth of porous alumina by Masuda and Fukuda [1] there has been an ongoing research effort to obtain porous alumina with an almost monodisperse pore diameter by self-assembly [2–5], lithography [6–9] or a combination of both [10]. For example, Nielsch et al. proposed that self-ordered porous alumina with any kind of interpore distance could be obtained when anodization conditions are in line with the 10% porosity rule [11]. In addition, several research groups have demonstrated the fabrication of monodomain porous alumina structures by anodization of lithographically pre-patterned Al exhibiting an extremely high aspect ratio [12,13]. Eventually, the fabrication of monodomain porous alumina with sub-100 nm diameter would be limited by the resolution of lithography [14]. Recently, we have suggested an alternative way to produce quasi-monodomain porous alumina with an interpore distance corresponding to 60% of the lattice constant of the master stamp, \( D_{\text{lattice}} \). Here, the method will be referred to as guided self-organization since pre-patterns formed by the master stamp not only play a role as seeds for the pore formation, but also help to guide pore formation in between the pre-patterns in a self-assembly manner [10].

As we have shown previously, anodization at 120 V in 0.17 M phosphoric acid allows the preparation of quasi-monodomain porous alumina with an interpore distance of 300 nm (Fig. 1(b), it was referred to as type B). Moreover, it turned out that an anodization strategy at 100 V in 0.17 M phosphoric acid (it was referred to as type A) was not successful in creating new pores in the middle of pre-patterns, corresponding to \( D_{\text{lattice}}/2 = 250 \) nm (Fig. 1(a)).

In this paper, we will propose a model to explain the guided self-organization. This model not only helps us explaining the fabrication of type B, but also improve our understanding of the general properties of ordered pore formation during anodization of aluminum.
Fig. 1. Schematic diagram of strategies for smart nano-imprint: (a) Type A (at 100 V); (b) type B (at 120 V). Large circles denote pre-patterns with a 500 nm distance, while small circles correspond to new pores resulting from the self-ordering of porous alumina during the anodization.

2. Experimental section

The fabrication process of quasi-monodomain porous alumina has been presented in detail elsewhere [10]. In brief, nano-imprinting was carried out with a master stamp having a lattice constant of 500 nm under a pressure of 5 kN/cm². Subsequently, anodization was performed under the optimum

Fig. 3. Formation of protective oxide boundaries, which are able to prevent the creation of pores inside the boundary. This is caused by suppression of the field-enhanced oxide dissolution on the areas where $\theta_{om}$ is smaller than 180°. (a) 40 V, (b) 90 V, (c) 100 V, (d) 116 V, (e) 130 V and (f) 155 V. Anodization conditions: 0.04 M oxalic acid at 2 °C. The circles in the insets indicate the boundary of protective barrier oxide.
conditions, for type A (100 V, 0.17 M H₃PO₄) and for type B (120 V, 0.17 M H₃PO₄). In some cases, oxalic acid solutions were used instead of phosphoric acid since it is more acidic. For example, anodization was performed at 40, 90, 100, 116, 130, and 155 V, respectively, in very dilute oxalic acid solution (0.04 M) to elucidate suppression of the field-enhanced oxide dissolution at the wedge. For the two-step anodization, the first-formed alumina oxide is dissolved in a solution containing chromic acid (CrO₃), as reported previously [1–5]. Subsequently, the porous alumina structures were characterized by scanning electron microscopy (SEM).

3. Mechanism

The mechanism of field-enhanced oxide dissolution is schematically shown in Fig. 2. When a potential is applied, an oxide layer is generated at the electrolyte/metal interface. Since the thickness (d) of the oxide formed at the initial stage is determined by applied potential with the proportionality constant of around 1.25 nm/V, the higher the applied potential, the thicker the film formed (see $d_1$ and $d_2$ of Fig. 2).

The pore nucleation theory, which is based on the field-enhanced oxide dissolution [5,15–18], claims that pores can be nucleated and developed only on those areas where the oxide/metal interface angle ($\theta_{ox/m}$) is larger than 180° (Fig. 2). Therefore, pores will start to develop at the tips of nano-imprinted inverted pyramidal pits at which the electric field is strongly focused (A of Fig. 2). Moreover, according to the linear stability theory [18], due to fluctuation of a non-flat oxide formed at the initial stage and the corresponding local electric field enhancement, pores are created in the areas between the nano-imprinted pits (C of Fig. 2). During the course of the pore growth, some of pores formed on the area C are going to vanish and merge together by self-ordering.

On the other hand, since the electric field cannot be concentrated on the areas where $\theta_{ox/m}$ is smaller than 180°, pore formation cannot take place at a wedge (B of Fig. 2). As the thickness of oxide films increases as a function of the applied potential, the circumference of the curvature of oxide formed at the wedge increases (B of Fig. 2). As a result, the areas in which pores can be developed, are reduced when the applied potential increases.

The protective oxide boundaries, suppressing the field-enhanced oxide dissolution, are shown in Fig. 3. For example, there is no pore formation inside the white circles (Fig. 3). Their average diameter of the protected area increases with increasing applied potential, e.g., from around 260 nm for 90 V to 500 nm for 155 V, when 0.04 M oxalic acid is used as the electrolyte. Note that if a weak electrolyte such as phosphoric acid is used, the diameter of the protected area is slightly increased. For instance, larger protected areas are observed in Fig. 4. This can be explained by the fact that the higher the pH value, the more difficult the nucleation of pores. Note that the pH value is strongly related to the potential threshold for field-enhanced dissolution at the pore tip [11,18].

Assuming that the oxide grown at the wedge of the pits suppresses the creation of pores due to the hindrance of the field-enhanced oxide dissolution, it is reasonable to assume the following: for type A, the diameter of protective oxide, which is originated from the wedge of pits, is not enough to guide the pore nucleation outside the protected area. In other words, the area in which field-enhanced oxide dissolution can occur is too broad due to a thin initial-oxide film at the wedge. For type B, the area in which pore nucleation can occur is restricted to the center of the nano-indentated pits (M1 of Fig. 5(a)) due to the large protected area for the field-enhanced oxide dissolution. This enables the guidance of a new pore (Fig. 5(b)). If the pores are fully developed in the center of the three pits by the guided self-organization, the cell orientation is turned by 30° relative to the original orientation (see the arrows in Fig. 5(a) and (b)).

In addition, it has to be mentioned that the pore arrangement can only be maintained up to around 1 µm for type B since the anodization conditions are not in the self-ordering regimes [11]. However, we expect that we can obtain much thicker quasi-monodomain porous alumina by the guided self-organization if the anodization is carried out in the self-ordering regimes.
4. Effects of the flatness of the substrate surface

One can expect that the interpore distance of the pore array can be further reduced to 36% (60% × 60%) of the lattice constant of the master stamp if a two-step process is adopted. For example, after a first reduction of the interpore distance by 60% by the guided self-organization (at 120 V), the first formed oxide is removed, followed by anodization at around 72 V. However, this strategy is not successful since there are preferred positions for the generation of pores in the scalloped patterns as shown in Fig. 6. For instance, M2 would be the ideal position for further reduction. However, for such a position, the pores are created on the shoulder of the scal-

Fig. 6. Suggestion for a strategy to further reduce the interpore distance to 36% of the lattice constant of the master stamp by a two-step guided self-organization (nano-imprint → anodization at 120 V → removing the oxide → anodization at 72 V) procedure. The strategy is not successful due to the surface roughness of the substrate after the first anodization. P2: pores formed by anodization at 120 V; M2: the ideal center of P2; P3: real pores formed by anodization at 72 V.

Fig. 7. SEM micrograph of triangular pores generated during the growth of pores by the guided self-organization at 120 V in 0.17 M phosphoric acid for 20 min (a). The corresponding schematic diagram is shown in (b–d). Triangular pores denoted by A of (d) are generated from the lithographic patterns with a square shape. B and C of (d) indicate triangular pores with a mirror shape of A of (d) and dot pores, respectively, both of which are generated by self-ordering.

Fig. 5. Mechanism of the guided self-organization. (a) The dotted circles signify the boundary in which the field-enhanced dissolution is suppressed. There is no pore formation by self-ordering inside the boundary. (b) Pores grow stable if the pores initiated by self-ordering are at a suitable position. Note that the direction of the cell is turned by 30°. P1: pores by the nano-imprint, P2: pores by the guided self-organization, M1: center of three nano-imprinted pits and the arrows indicate direction of the cells.
lops during the second anodization ($P_2$). This is also cor-
related with the protected area for the field-enhanced oxide
dissolution at the wedge. Since $\theta_{o/m}$ is less than 180$^\circ$ at the
points of $M_2$, pores are generated at $P_3$ rather than $M_2$. This
underlines the importance of surface flatness for the guided
self-organization.

5. Triangular pores

The development of triangular pores using a master
stamp with a honeycomb structure lattice was reported by
Masuda et al. [19]. Herein, without specific pre-patterns
designed for the triangular pore formation, pores with a
triangular shape are observed during the growth of pores by
the guided self-organization (Fig. 7(a)). The triangular pores
are not formed homogeneously on the entire area since the
nano-imprinted patterns on the surface are not identical in
size and depth. Mechanism of the formation of the triangular
pores is schematically shown in Fig. 7(b)–(d). Pores are
created in the nano-imprinted pits (Fig. 7(b)). Subsequently,
pore formation by self-ordering takes place at the center of
three nano-imprinted pits (Fig. 7(c)). Although more than
one pore can be nucleated at some points, only one of them
would survive during anodization by self-ordering. From
Fig. 7(a), it is reasonable to assume that the larger triangular
pores originate from the pre-patterns with a rectangular shape
(A of Fig. 7(d)). Then, pores newly formed by self-ordering
become a mirror shape of the triangular pores as pores grow
due to an interaction between them (B of Fig. 7(d)). In
addition, pores with a dot shape are exhibited in the center of
six apexes of triangular pores (C of Fig. 7(d)). We suppose
that if these dots are fully developed into circular pores,
whose sizes are equal to the sizes of the pores generated
from triangular pores, quasi-monodomain porous alumina is
achieved. However, it is often observed that some dots would
vanish due to a strong interaction between the triangular
pores, resulting in a disordered arrangement on the bottom
of pore arrays. In addition, it is still a remaining question to
explain what determines the direction of triangular pores,
which are developed from square pre-patterns, e.g., inverse
triangular pores as shown in Fig. 7 or triangular pores.

6. Conclusions

Guided self-organization enables lithographical methods
to prepare quasi-monodomain porous alumina having an in-
terpore distance smaller than that of the lattice constant of
the master stamp. The mechanism of guided self-organization
can be explained by protective oxide boundaries formed at
the wedge and a nucleation of pores outside the protective
oxide by self-ordering. We demonstrated that the surface flat-
ness plays an important role to produce quasi-monodomain
porous alumina by the guided self-organization. In addition,
pores with triangular pores were explained as a result of an
interaction between pores created by lithography and by self-
ordering.

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