

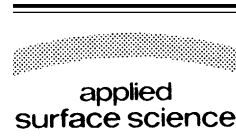


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Applied Surface Science 219 (2003) 282–289



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Self-assembled stripes on the anodic aluminum oxide by atomic force microscope observation

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Received 17 February 2003; received in revised form 7 May 2003; accepted 7 May 2003

Abstract

Non-polished aluminum sheets were anodized. The nanostructures were investigated in details using an atomic force microscope (AFM). The coexistence of self-assembled stripes and porous arrays on the Al surface was observed. The formation mechanism of the stripes is discussed based on the Brusselator model. We suggest that the self-assembled patterns on the Al surface strongly depend on the competition of the formation and the dissolution rate of alumina film during the reaction process. It is also found that this type of ordered structure can only form in certain conditions.

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PACS: 68.37; 81.16; 82.45

Keywords: Anodic aluminum oxide (AAO); Atomic force microscope (AFM); Brusselator model

1. Introduction

Ordered nanodots, nanotubes and nanowires have received considerable attentions over the past decades because of their unique electronic, optoelectronic properties, and they also play an important role in future nanodevices [1–4]. These nanostructures can be prepared using a common template, viz. porous anodic aluminum oxide (AAO) [5–8]. After anodic oxidation in oxalic acid or sulfuric acid with definite concentration, the annealed highly pure aluminum sheet can spontaneously form a regularly arranged porous structure with controlled diameters. This is a typical self-assembled ordered structure. However, during elec-

troplishing process, ordered stripes and hexagonal dots on the aluminum surface can also form [9–14]. Ricker et al. [12] obtained ordered stripes with uniaxial symmetry at cell voltage $E = 30\text{--}50$ V, ordered dots with hexagonal symmetry at $E = 55\text{--}65$ V, and random structures outside this potential window ($E < 30$ V and $E > 65$ V) by electropolishing polycrystalline Al film for 10–30 s. Konovalov et al. [10] observed that the ordered stripes with large area coverage could only form on the Al(1 0 0) surface. In our paper, non-polished AAO samples have been prepared under different conditions. Their topographies are investigated using an atomic force microscopy (AFM). Using the Brusselator model, we suggest that the stripe formation depends not on polar molecules in electrolyte but on the competition between the formation and the dissolution rate of alumina in the reaction process.

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2. Experiments

High purity Al sheets (Puratronics, 99.998%) were rinsed in alcohol and subsequently ultrasonically in de-ionized water for 3 min. After that, they were put into NaOH solution to degrease for 3 min, and then rinsed again in de-ionized water. This non-polished Al sheet was used as the anode and a graphite rod as the cathode. The anodization process would create porous alumina film on the Al surface with a regimented, hexagonal close-packed arrangement. This reaction was carried out under a constant voltage in 0.3 ML $\text{H}_2\text{C}_2\text{O}_4$ or 1 ML H_2SO_4 for 1 h at room temperature. For H_2SO_4 , the anodic voltage varied from 15 to 30 V, and for $\text{H}_2\text{C}_2\text{O}_4$, from 40 to 55 V. Each sample was prepared with a voltage step per 5 V. The anodized size of Al sheet was about 1 cm \times 1 cm, and the anodized current is about 30–40 mA. All as-treated samples were cleaned in de-ionized water and then dewatered by alcohol. The topographies were obtained by AFM at room temperature (Digital Instrument Nanoscope IIIa, in Tapping mode).

3. Results and Discussions

The obtained AAO template has two characteristics. One is the pore array with controllable diameter. When the anodic voltage in $\text{H}_2\text{C}_2\text{O}_4$ electrolyte increases from 40 to 55 V, the pore diameters increase from 20 to 40 nm. The pore size distribution is more uniform in $\text{H}_2\text{C}_2\text{O}_4$ than in H_2SO_4 . The other characteristic is the existence of stripes at nanometer scale over the pore arrays. However, the stripes do not form along the pore edges or other well-regular directions, and there is no direct relation that could be found among them. Fig. 1a and b gives the height image and phase image of our samples by AFM, respectively. The stripe and pore edges can be seen clearly separated in the phase image. The surface of Al samples in our experiments has more roughness, and even some big pits in micrometer depth can be seen. By random choosing the scanning area, it reveals that the stripes can appear anywhere on Al surface, as shown in Fig. 2a. However, the fluctuated topography on the surface has significant influence on the stripe trend, and the stripes on the flat areas are denser than in deep pits. From the zoomed image in Fig. 2b, we can see

that the stripes have uniform and network-like pattern, where the white arrows denote the tips of the stripes. In Fig. 2c, a cross-section along the white line in Fig. 2b indicates that the stripes have uniform diameter and their height is about 40 nm.

In order to explain the formation kinetics of these stripes, [13] suggested that an interfacial instability, possibly caused by the preferential adsorption of polar organic molecules on surface ridges, may be responsible for the pattern formation. The preferential adsorbates, due to their diffusion on the surface and the resulting shielding effects, reduce the dissolution rate on surface maxima. But the field-assisted dissolution mechanism, which is controlled by the transport of ions through the hydrodynamic diffusion layer, enhances the local dissolution. As a result of the two opposite mechanisms, stripe patterns can form under special conditions. The authors of [10] could not correlate the observed nanostripe structure with the crystal structure of Al, so they finally pointed out that the preferential adsorption of polar molecules and selective dissolution caused by mechanical stress may be the reasons for the stripe formation. It should be noted that both papers have considered the contributions of polar molecules. However [15] indicated that similar ordered stripes at oxide film/metal interface of aluminum could also appear under certain conditions without the presence of an electrolyte. It means that the polar molecules in electrolyte are not as necessary for the pattern formation.

From our point of view, the competition between the dissolution and the formation rate of oxide layer on Al surface should play an important role for the formation of such self-assembled structures on AAO surface. A common feature for the anodic oxidation in this paper and the electropolishing in [13] is the existence of the oxide film on the Al surface with H^+ ions in electrolytes that are involved in the main reactions. We propose that both self-assembled stripes are affected by the same kinetics mechanism with the participation of H^+ ions.

While the structure and composition of the oxide film on the Al surface is sophisticated and hard to identify, the most accepted opinion is that it is amorphous and tends to crystallize to $\gamma\text{-Al}_2\text{O}_3$ [16], and other possibly existing compositions include $\text{Al}(\text{OH})_3$, AlOOH and $\gamma'\text{-Al}_2\text{O}_3$ [17]. As shown in Fig. 3, the anode Al loses electrons under an electric field and

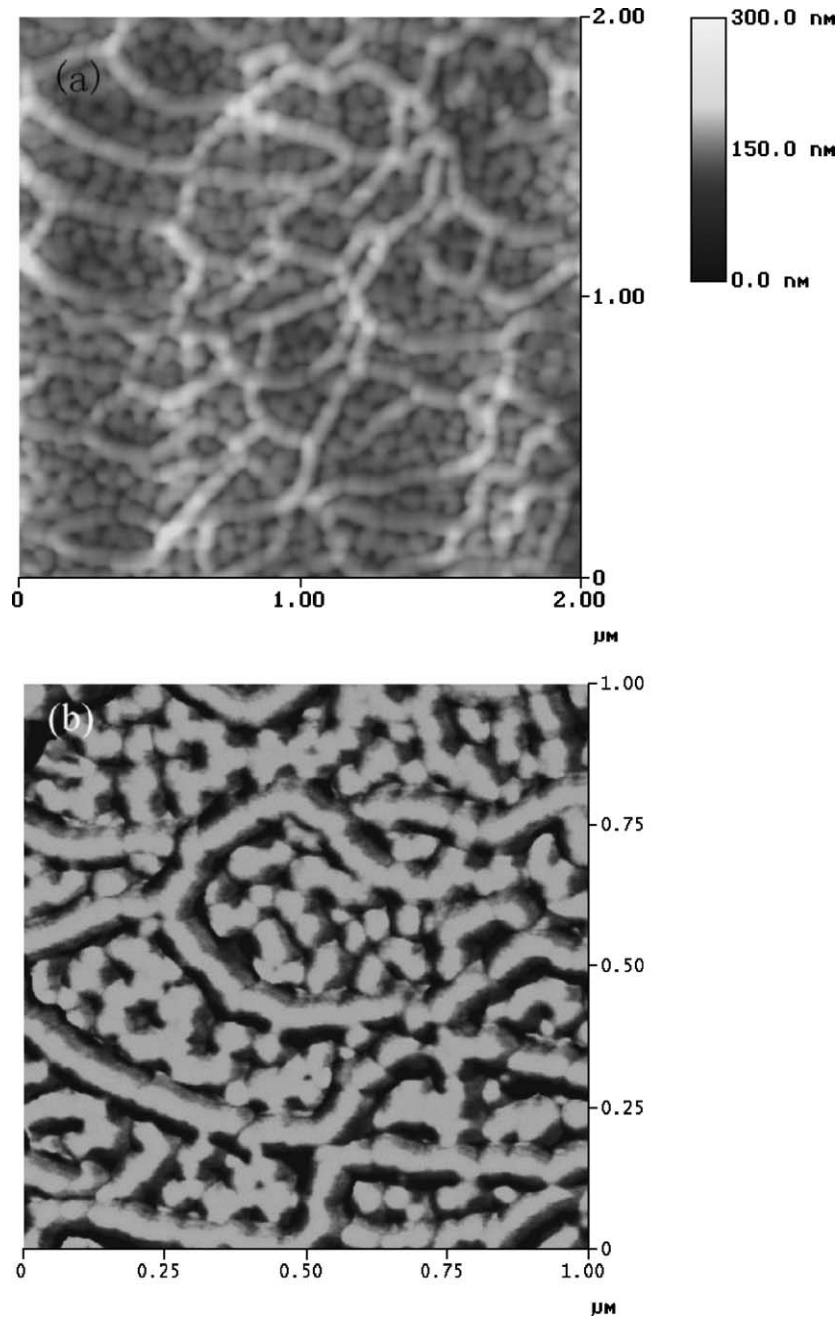


Fig. 1. Structure of the self-assembled stripes with pore arrays on the non-polished AAO template; (a) AFM height image; (b) AFM phase image.

becomes Al^{3+} ion that will migrate from the inside metal into surface oxide film, and one half of them migrate to the electrolyte interface. They associate with oxygen ions from the electrolyte by water-split-

ting reaction and form oxide, shifting the oxide/electrolyte interface into the electrolyte. The same charge is transported by oxygen ions to the metal/oxide interface and compensates the other half of the metal

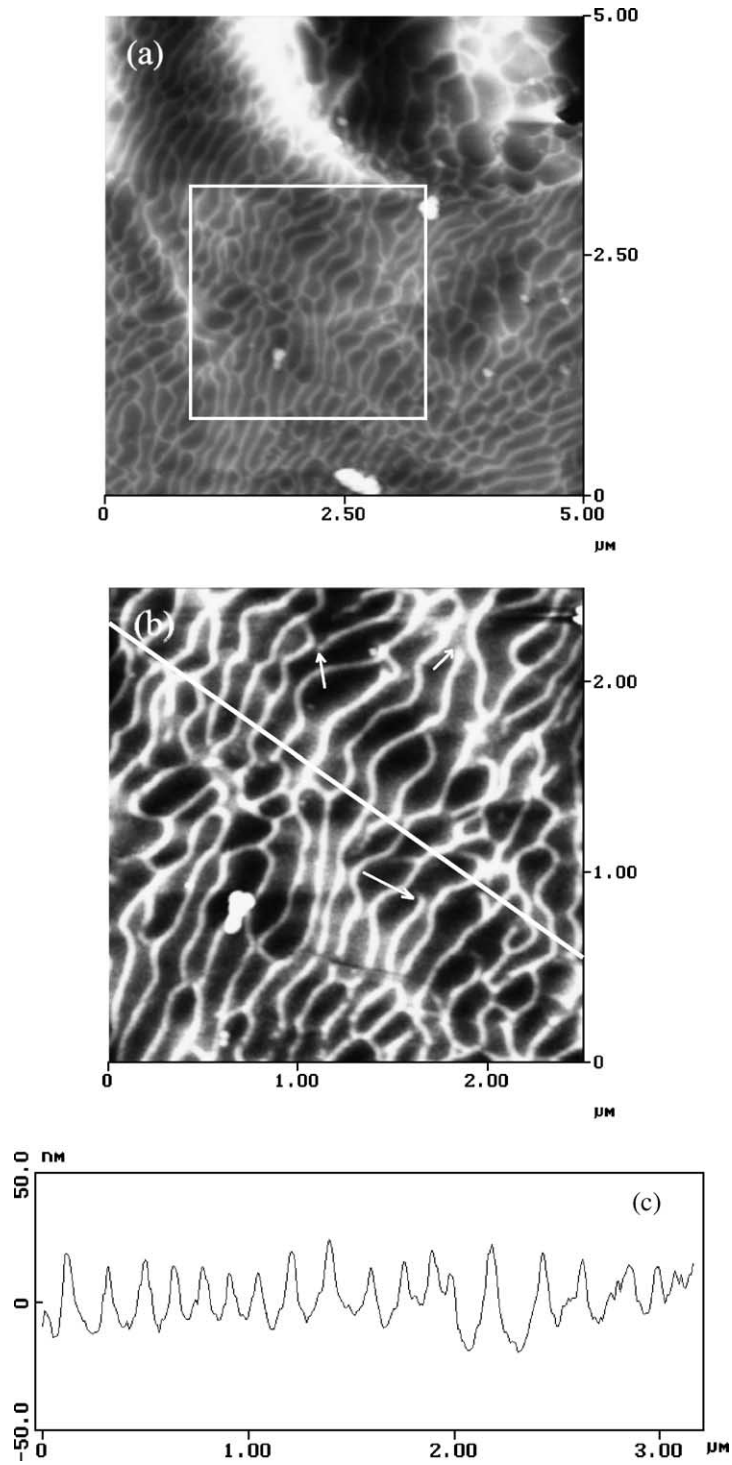


Fig. 2. A common stripe structure of the stripes on AAO template; (b) is a zoomed image of white square denoted in (a), (c) is a cross-section along the white line in (b).

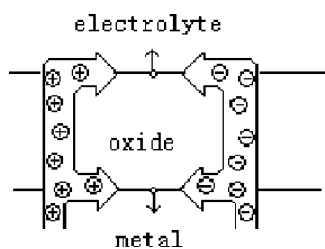


Fig. 3. Schematic representation of oxide growth at electrolyte/oxide interface.

ions. Metal is consumed and the oxide grows into the metal as well [17]. On the other hand, Al_2O_3 oxide is induced to dissolve by proton ions in electrolyte at the same time. These two reaction process are opposite, i.e. the formation and the dissolution of Al_2O_3 at oxide/electrolyte interface that can be described as following:

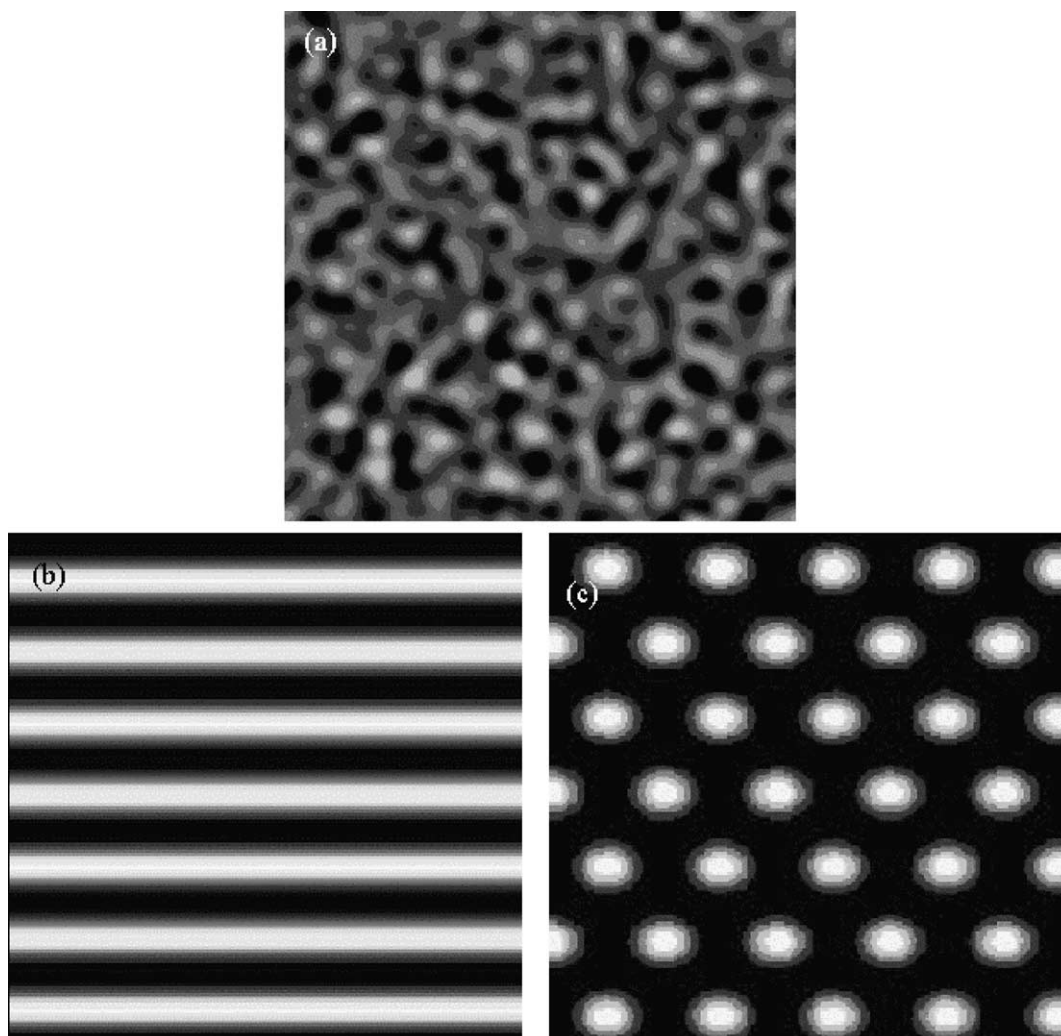
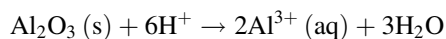
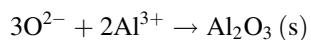
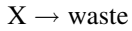
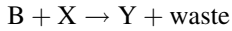


Fig. 4. Numerical simulations for a reaction–diffusion system based on the Brusselator reaction scheme. The diffusion coefficients for X and Y are fixed to 0.16 and 0.8, respectively. The input of A is 2.5, while the input of B is 5.24 in (a) for a common pattern, 5 in (b) for an ordered stripe pattern, 7 in (c) for an ordered dot pattern, respectively.

This is a kind of autocatalytic, non-equilibrium dynamic process. We note that the chemicals of Al_2O_3 (Al^{3+} in oxide) and Al^{3+} (Al^{3+} in aqueous solution) are both inputs and outputs of the reaction. Therefore, it can be described by Brusselator model [18]. A reaction-diffusion system based on the Brusselator reaction scheme can be presented as following:



Here, for our case, the chemical species X, Y can correspond to Al_2O_3 and Al^{3+} , respectively, while the chemical species A and B that can be treated as O^{2-} and H^+ have the fixed concentrations and do not change over time. The waste products have no influence on the reactions. For other chemical species, the detailed reaction functions can be found in [6]. The diffusion coefficients of X and Y are fixed, and only A and B are varied during the simulations. In the initial simulation, a random concentration distribution for Al_2O_3 and Al^{3+} is chosen, and then a macroscopic order structure will be evolved from chaos. Images in Fig. 4 are the results of numerical simulations and show the change of concentration of the specie Al_2O_3 with different parameters. Fig. 4a shows a typical pattern according to the Brusselator model. While both stripe pattern in Fig. 4b and dot pattern in Fig. 4c (Turing patterns) reveal ordered bistable patterns formed in the autocatalytic reaction system at some suitable conditions that do not need the assistance of the polar molecules in electrolyte as explained in [13]. From this model, the patterns on Al surface strongly depend on the reaction conditions, such as electrode voltage, anodic time, annealing temperature [19], local potential, and composition concentration, etc. All of those will affect the dissolution and the formation rate of Al_2O_3 as evidenced by our experiments. Also, in accordance with the simulations, the varied values of diffusion coefficients of A and B will greatly affect the behavior of the model. In a simple way, the concentration of the species can be thought directly correlated with the height of surface structure that are determined by AFM. The mathematical transition between them can be referred to [13]. However, this is only a very simple simulation for a reaction–

diffusion system, and a lot of work still needs to be done to explicate the formation mechanism. Fig. 2 shows a common stripe structure on the AAO surface. Fig. 5 shows some special observed shapes of the stripes. In Fig. 5a, large area dendrite propagation is found, while in Fig. 5b, a tangled ribbon-like structure, of 100 nm width and 10 nm height, is shown. Both of them reveal some fractal characteristics, and the effect

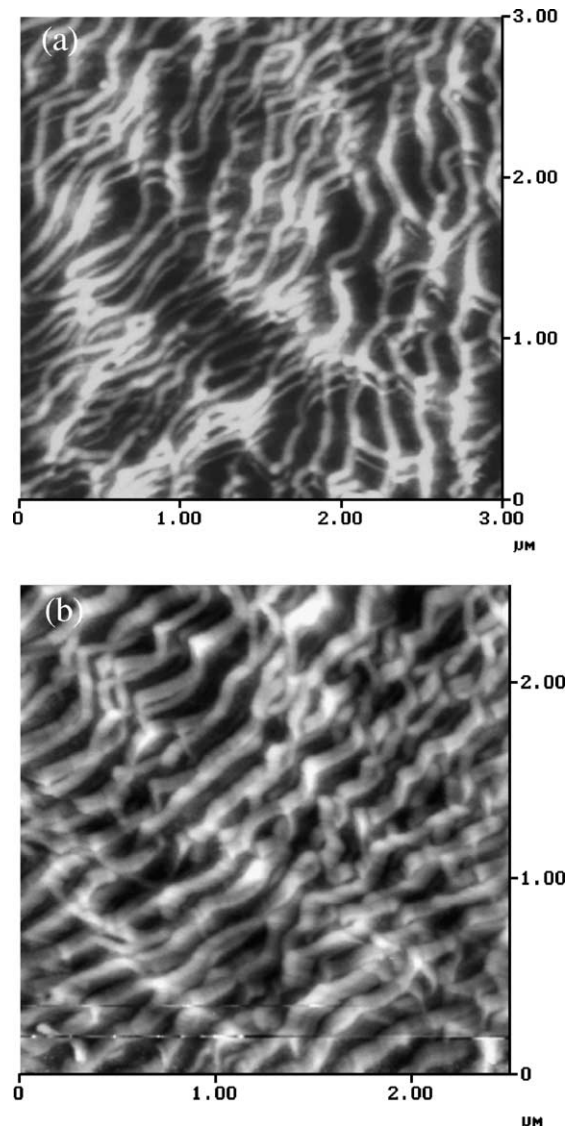


Fig. 5. Some unusual stripe structures; (a) a dendrite propagation structure; (b) a tangled ribbon-like structure.

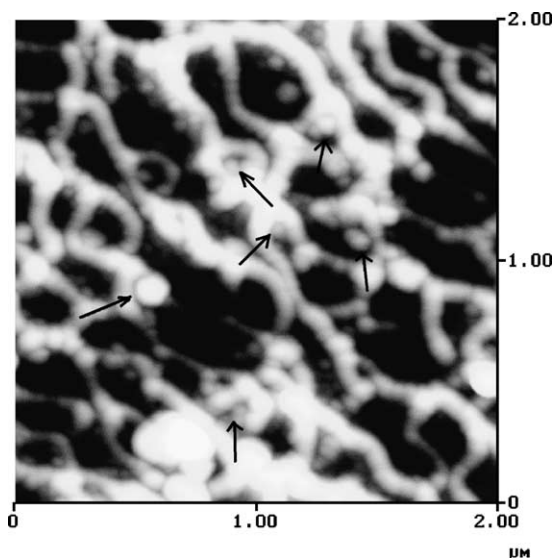


Fig. 6. Stripes crossing the clusters during the oxide film growth. The black arrows denote the cluster interrupter.

induced by multi tips of AFM can be excluded after further observing the details. These fractal patterns can be induced by local disturbance at electrolyte/oxide interface. As shown in Fig. 6, the formation of the stripes can take a way of either detouring or stopping around the big grains during the oxide film growth because of the rough Al surface, and the black arrows denote the clusters as interrupters.

It should be noted that in our experiments the net-like stripes on AAO samples have already existed when anodic voltage is 15 V. However, the diameter of pores under these stripes is hard to be resolved by AFM probe. With anodic voltage increasing, the diameter of pores increases, too. We suggest that before the pore formation, the reaction at the electrolyte/oxide film interface is responsible for the self-assembled stripes. Once pores have been generated, electric field will become the highest at the center or close to the center of the pore bottom [6], so the current can go through the pores, and it causes deepening and widening of the pores. Pore deepening becomes dominant. From the above point of view, the coexistence of self-assembled stripes and porous arrays on the Al surface is understood.

The width of the self-assembled stripes on the Al surface by electrochemical method has reached nanos-

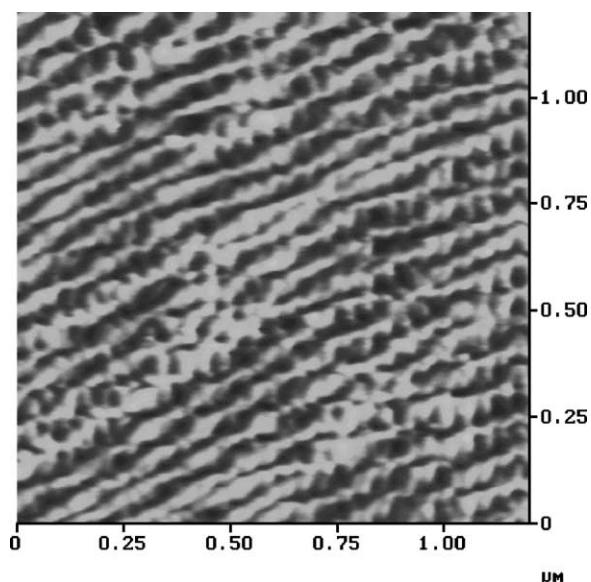


Fig. 7. Ordered stripes together with pores in AAO film by exactly controlling experiment parameters.

cale that it is better than the conventional photolithography or electronic beam lithography. The ordered stripes can be used as a two-dimensional template to prepare nanotubes or nanowires. And metal stripes can be served as conducting wires or electrodes in nanodevices. Moreover, the stripe formation by self-assembly is a dynamic process, and the ordered stripes together with hexagonal pores in AAO film, as shown in Fig. 7, could be obtained through exactly controlling parameters in the experiments, therefore, this method can provide a new pathway to prepare a new template with more complex nanostructures.

4. Conclusion

In this paper, the high purity and non-electropolished Al sheets have been anodized and their topographies have been investigated by AFM. The results show that AAO has self-assembled stripes on the pore arrays. The oxide film on Al surface, not polar molecules as proposed in [13], plays an important role for the pattern formation. As a reaction–diffusion system, we use a Brusselator model to simulate these ordered patterns and find that they depend on the competition between the formation and the dissolution rate of

Al₂O₃ during the reaction process, and this is a non-equilibrium process. The high ordered patterns can only appear in a narrow parameter range.

Acknowledgements

This project is supported by National Natural Science Foundation of China under Grant Nos. 60071009 and 90206028. The authors are grateful to Prof. M. Wang (Department of Physics, Nanjing University) for useful discussions.

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