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ORIGINAL PAPER

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Patterning polycrystalline aluminum by electropolishing at low voltages

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Abstract Highly ordered stripes with controllable spacing of the pattern lines are obtained during electropolishing aluminum (Al) foils at low voltage. The samples are investigated in detail with the Atomic Force Microscope (AFM). Stripes with similar spacing of the pattern lines are observed on the surface of Al sheets which are electropolished in the same electrolyte at various voltages. However, the spacing of the pattern lines is closer when there is more ethanol in the electrolyte at the same voltage. The formation mechanism of stripes with dissimilar spacing of the pattern lines in different electrolyte is discussed. We suggest that the spacing of the pattern lines depends on the concentration of the polar molecules (ethanol) in the electrolyte.

Keywords Electropolishing · Stripes · Electrolyte · Atomic Force Microscope

Introduction

Using ordered surface patterns at the nanometer scale, one can fabricate magnetic [1] or semiconductor [2] nanostructures for new devices by either direct deposition or replication. The methods currently used in nanoscale patterning include electron-beam lithography, focused ion-beam etching, and scanning-probe-based writing. At the nanometer scale, these methods have several disadvantages, e.g. high cost, slow throughput, and high susceptibility to errors. As such, these methods are controllable but not cheap. An alternative approach has been investigated utilizing the self-organized (or self-assembly) phenomenon observed in some materials systems. Self-ordering processes can produce highly ordered patterns, although the pattern-scale is not usually controllable. Therefore, the self-ordering of nanoscale structures with controllable pattern-scale would be very desirable.

After oxide formation during cycles of heating and cooling, nanoscale topographies were first obtained on aluminum (Al) [3]. The annealed highly pure Al sheet can spontaneously form a regularly arranged porous structure with controlled diameters after anodic oxidation in oxalic acid or sulfuric acid with a specific concentration [4]. This is a typical ordered structure [5]. In striking contrast with this slow pore growth is the rapid self-ordering produced by electropolishing [6–15], which is a fast anodic dissolution on the metal immersed in a suitable electrolyte. Yuzhakov et al. [10] obtained perfectly periodic stripes and hexagonal hill patterns within a small voltage window, and the spacing of the pattern lines was about 80 nm. In our paper, highly ordered stripes have been obtained at lower electropolishing voltage than in other reports [7, 10]. Using AFM we found that the stripes have similar spacing of the pattern lines when the Al foils are electropolished in the same electrolyte even if obtained at the same voltage; and the spacing of the pattern lines is closer with more ethanol in the electrolyte. Thus we can control the spacing scale of the pattern lines by changing the concentration of the electrolyte. The formation mechanism of the stripes with different spacing of the pattern lines in a different electrolyte is discussed. In our view, the spacing of the pattern lines depends on the ethanol concentration in the electrolyte.

Experiments

Al sheets with a purity of 99.99% were annealed at 500 °C for 2 h. The Al sheets were washed ultrasonically in toluene to degrease for 3 min and subsequently rinsed in de-ionized water. They were then put into NaOH solution (1 M) for 1 min to remove the oxide on the Al surface, then rinsed again in de-ionized water. The Al

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sample (1 cm×2.5 cm×0.3 mm) was used as the anode, then electropolished in electrolyte for 180 s at room temperature using a Pt sheet as counter electrode in the cell which we ourselves made. The electropolishing voltage was 10, 12 and 15 V, separately. The electrolyte we used were of three kinds: 'electrolyte one' consisting of 60 vol.% ethanol (analytical reagent) and 40 vol.% perchloric acid (72%), 'electrolyte two' consisting of 70 vol.% ethanol and 30 vol.% perchloric acid and 'electrolyte three'' consisting of 80 vol.% ethanol and 20 vol.% perchloric acid. The Al surface was imaged with the Atomic Force Microscope (AFM, P47-SPM-MDT, made in Russia).

Results and discussion

Figure 1 shows the AFM images of stripes that are produced on the Al surface by electropolishing for 180 s at 10, 12 and 15 V in different electrolytes. The voltage we used in the electropolishing process was lower than that in the works of Yuzhakov et al. [10] and Konovalov et al. [7], and the stripes are uninterrupted and highly ordered in all the images. The stripes have similar spacing of the pattern lines when the electrolyte is the same in each rank image but at different electropolishing voltage. They can transit through the rough surface of the sample, and the stripe disfigurement exists at this raised or sunk sites. FFT results of (a_1) (b_1) and (c_1) show there are two dots on the 45° and 135° direction of each FFT image. The dots reflect the finer scale contribution from the spacing of the pattern lines and the orientation of the stripes while the periodicity direction is along AB, CD and EF, separately.

Figure 2 gives the cross-section along the line AB, CD and EF. All their amplitudes are near 2 nm. They have, however, different average spacing of the pattern lines: 105, 75 and 35 nm. The samples are produced in 'electrolyte one', 'electrolyte two' and 'electrolyte three', separately. The spacing of the pattern lines is closer when there is more ethanol in the electrolyte. In the works of Yuzhakov et al. [10] and Konovalov et al. [7] the spacing of the pattern lines of all the stripes they showed is about 80 nm, nearly the same as the scale of the stripes we obtained by electropolishing in 'electrolyte two'. The voltages are lower in our experiments, but we obtained the stripes with the same spacing of the pattern lines. The electrolytes they used are all commercial containing 70.0 vol.% ethanol,10 vol.% 2-butoxythanol, 13.8 vol.% de-ionized water, 6.2 vol.% perchloric acid. The concentration of ethanol in commercial electrolyte is nearly the same as 'electrolyte two'. It indicates that the spacing of the pattern lines depends on the concentration of the electrolyte, not on the eletropolishing voltage.

In our opinion, the concentration of polar molecules affects the spacing of the pattern lines. The mechanism of electropolishing in the presence of polar molecules [10] suggested that an interfacial adsorption of polar organic molecules on the 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,

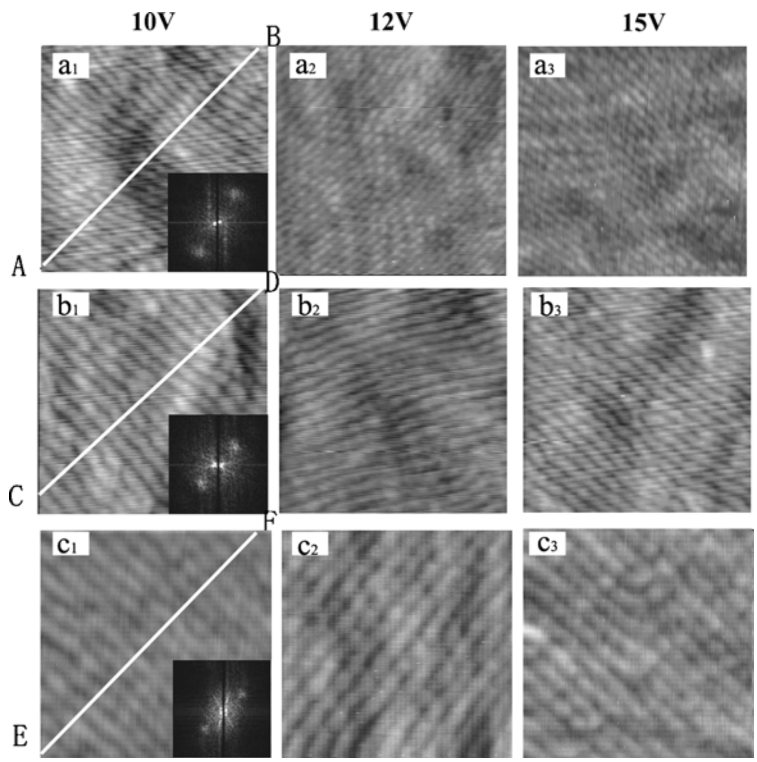

Fig. 1 AFM images of stripes that are produced on Al surface by electropolishing under various voltages for 180 s in different electrolyte: (a_1) (a_2) (a_3) 2000×2000 nm, in 'electrolyte one'; (b_1) (b_2) (b_3) 1000×1000 nm, in 'electrolyte two'; (c_1) (c_2) (c_3) 500×500 nm, in 'electrolyte three'. The result of 2D FFT analysis in (a_1) (b_1) (c_1) are shown as insert

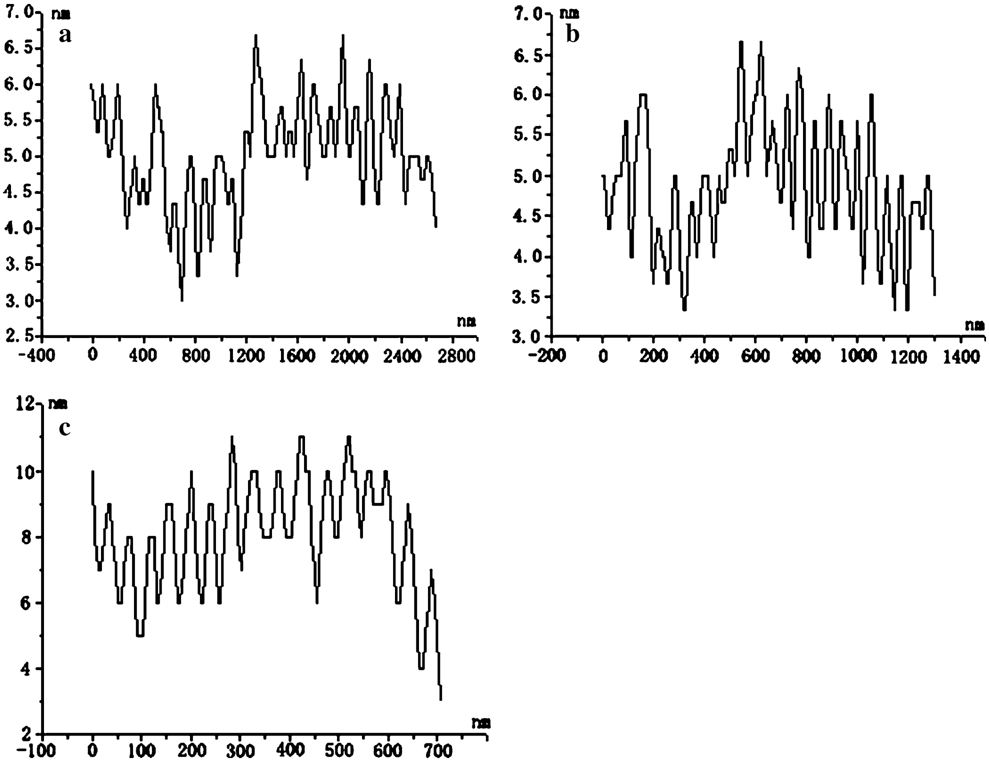

Fig. 2 Depth profile observed: (a) along the AB line in Fig. 1. (a_1); (b) along the CD line in Fig. 1. (b_1); (c) along the EF line in Fig. 1. (c_1)

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 condition. So the number of polar molecules adsorbed on the Al surface can affect the spacing of the pattern lines.

Our electrolyte contains the polar molecule, ethanol, and water molecules. There is much more ethanol than water molecules and most of the polar molecules in our electrolyte are ethanol. So ethanol is the representation of polar molecules in our paper. As shown in Fig. 3 we suppose that the 'hills' are Al atomics, and the order of the ethanol concentration in the three electrolyte is $a < b < c$. Perturbations to the interface increase in the electric field on the 'hill' relative to the 'valleys'. The higher electric field at the hills increases the dissolution rate, but also increases the adsorption rate of surfactants [10, 12]. After being given a positive voltage, the Al surface adsorbs ethanol molecules at the beginning of the electropolishing process. The order of the ethanol molecule amount on the Al surface is $a < b < c$. (We suppose one Al atomic adsorbs one ethanol molecule in situation 'c'. The polar molecules are the closest in this situation, which nevertheless is almost impossible.) When the ethanol adsorbed on the Al surface is more, there are less ions transporting through the hydrodynamic diffusion layer into electrolyte for shielding effects. So the ethanol adsorbed on the Al surface is closer, the spacing of the pattern lines after electropolishing is more open. The order of the spacing of the pattern lines is $a > b > c$.

Conclusion

In this paper, high purity Al sheets have been electropolished in different electrolytes and their stripes have been investigated by AFM. The results show that even at low voltage we can obtain stripes on Al foils. The stripes have different spacing of the pattern lines when the concentration of ethanol in the electrolyte changes. The polar molecules (ethanol) play an important role in the stripes formation, so when their concentration in electrolyte changes the spacing of the pattern lines also

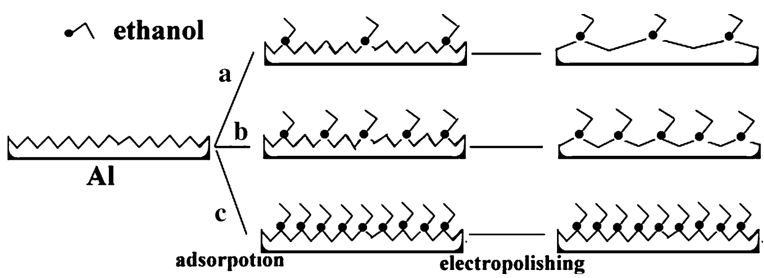

Fig. 3 Schematic of the formation of stripes with various spacing of the line pattern: (a) electropolishing in 'electrolyte one'; (b) electropolishing in 'electrolyte two'; (c) electropolishing in 'electrolyte three'

changes. Using this phenomenon we can produce highly ordered stripes with controllable scale. Highly ordered stripes with various spacing of the pattern lines can be obtained by changing the concentration of polar molecules in the electrolyte. It is more advantageous than electron-beam lithography and focused ion-beam etching in nanoscale. Konovalov et al. [7] have also shown that ordered stripes with large area coverage could only form on the Al (110) surface. The Al foils in our experiments are polycrystalline, so the highly ordered patterns can only appear in a narrow parameter range.

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