CHEMISTRY OF MATERIALS

VOLUME 11, NUMBER 8 AUGUST 1999

© Copyright 1999 by the American Chemical Society

Communications

Highly Ordered Nanotopographies on Electropolished Aluminum Single Crystals

V. V. Konovalov[‡,§] G. Zangari,[†,||,⊥] and R. M. Metzger*[,†,‡]

Center for Materials for Information Technology and Departments of Chemistry and Metallurgical and Materials Engineering, The University of Alabama, Tuscaloosa, Alabama 35487

Received March 9, 1999
Revised Manuscript Received June 17, 1999

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. At these length scales, lithography has several disadvantages, e.g. the high cost of making and replicating electron beam-generated masks, the slow throughput due to the sequential nature of the process, and the high susceptibility to errors. Self-ordering processes can produce highly ordered patterns, which however do not usually extend over large areas. Long-range self-ordering of nanometer-scale structures would thus be very desirable.[3]

Nanoscale topographies were first obtained on Al after oxide formation during cycles of heating (400−660 °C) and cooling, with the formation of hexagonal or lamellar structures.[4,5] Highly ordered hexagonally arranged pores can also be obtained by anodizing Al in acid for several hours, with pore formation, then chemically removing this porous oxide and re-anodizing: pores with perfect hexagonal ordering and 60−200 nm pore-to-pore spacing form in domains a few micrometers in size.[6−10] In striking contrast with this slow pore growth is the rapid self-ordering produced by electropolishing, which is a fast anodic dissolution of the metal immersed in a suitable electrolyte.[4,11−14] By electropolishing polycrystalline Al films[11,12] or foils[12,13] for 10−30 s, ordered topographies with uniaxial symmetry (stripes) or hexagonal symmetry (mounds) were reported within 1−2 μm domains: stripes were obtained at cell voltage $E = 30-50$ V, hexagons at $E = 55-65$ V, and random structures outside this potential window ($E < 30$ and $E > 65$ V). These structures were implicitly assumed to be the same for all crystal grains.[11−13] Assuming a preferential adsorption of organic molecules on surface ridges and diffusion control for the reactive species led

---

[*] E-mail: rmetzger@bama.ua.edu.
[†] Center for Materials for Information Technology.
[‡] Department of Chemistry.
[§] E-mail: vvk01@bama.ua.edu.
[||] Department of Metallurgical and Materials Engineering.
[⊥] E-mail: gzangari@coe.eng.ua.edu.

(1) Chou, S. Y. *Proc. IEEE* **1997**, *85*, 652.
(2) Miller, D. A. B.; Chemla, D. S.; Damen, T. C.; Wood, T. H.; Burrus, C. A.; Gossard, A. C.; Wigemann, W. *IEEE J. Quantum Electron.* **1985**, *21*, 1462.
(3) White, R. L.; New, R. M. H.; Pease, R. F. W. *IEEE Trans. Magn.* **1997**, *33*, 990.
(4) Hirsch, P. B. In *Progress in Metal Physics*; Chalmers, B., King, R., Eds.; Pergamon Press: London, 1956; p 236.
(5) Doherty, P.; Davis, R. S. *J. Appl. Phys.* **1963**, *34*, 619.
(6) Masuda, H.; Satoh, M. *Jpn. J. Appl. Phys. Part 2* **1992**, *31*, L1775.
(7) Masuda, H.; Fukuda, K. *Science* **1995**, *268*, 1466.
(8) Zhang, L.; Cho, H. S.; Li, F.; Metzger, R. M.; Doyle, W. D. *J. Mater. Sci. Lett.* **1998**, *17*, 291.
(9) Jessensky, Q.; Müller, F.; Gösele, U. *Appl. Phys. Lett.* **1998**, *72*, 1173.
(10) Li, F.; Zhang, L.; Metzger, R. M. *Chem. Mater.* **1998**, *10*, 2473.
(11) Ricker, R. E.; Miller, A. E.; Yue, D.-F.; Banerjee, G.; Bandyopadhyay, S. *J. Electron. Mater.* **1996**, *25*, 1585.
(12) Bandyopadhyay, S.; Miller, A. E.; Chang, H. C.; Banerjee, G.; Yuzhakov, V.; Yue, D.-F.; Ricker, R. E.; Jones, S.; Eastman, J. A.; Baugher, E.; Chandrasekhar, M. *Nanotechnol.* **1996**, *7*, 360.
(13) Yuzhakov, V. V.; Chang, H.-C.; Miller, A. E. *Phys. Rev.* **1997**, *B56*, 12608.

10.1021/cm990144g CCC: $18.00 © 1999 American Chemical Society
Published on Web 07/24/1999

to a strong theoretical dependence of the pattern on the applied voltage.[13]

We electropolished Al single crystals to study the effect of surface defects and crystalline orientation on pattern formation and on the degree of long-range order. High-purity (Puratronics, 99.998%) polycrystalline Al sheets (0.25 mm thick) and rods (10 mm across, 6 mm thick) were used, as well as monocrystalline Al rods (Monocrystals, 99.999+%, 10 mm across, 6 mm thick) with (111), (110), and (100) orientations. The electropolisher was a Buehler Electromet 4 apparatus; the electropolishing solution, flowing from cathode to anode at 15 °C, was a mixture of 70 vol % ethanol, 10 vol % 2-butoxyethanol, 13.8 vol % water, and 6.2 vol % perchloric acid, similar to solutions used elsewhere.[11−13] Al rods were mechanically ground down to 1200 mesh, and polished with 0.5−3 μm diamond paste. Both Al sheets and rods were rinsed with acetone, washed for 20 s in 5% NaOH (60 °C), immersed for 1 s in 35% HNO_3, and rinsed with deionized water. Surface topography was recorded by atomic force microscopy (AFM) on a Digital Instruments Dimension 3000 microscope.

Continuous electropolishing of polycrystalline Al at a constant voltage of 20−40 V for 30−60 s produced surfaces with root-mean-square roughness about 1−4 nm. Above 50 V, the surface was severely damaged. To avoid this damage, we thereafter applied voltage not continuously, but in pulses of 5 s duration, each followed by a cooling period of 10−15 s.

AFM images of pulse-electropolished polycrystalline Al showed different topographies on different crystalline grains of the same sample. For example, regular stripes were observed for only 10−20% of the grains of a sample. Using Al single crystals in later experiments eliminated the uncertainty related to grain distribution.

An example of patterns near a grain boundary of polycrystalline Al is shown in Figure 1. There are different patterns on the two sides far from the boundary. The depth profile shows a preferential etching at the grain boundary. The preferential etching seen here in pulsed electropolishing suggests that polycrystalline Al dissolves not under transport (diffusion) control[14] but rather under charge transfer control, with preferential dissolution of high free-energy sites, such as grain boundaries. As further evidence, current transients obtained during electropolishing (not shown) demonstrate that a steady value for the current is established only after about 30 s.

Typical AFM images of (111), (110), and (100) Al single crystals, electropolished for 6 × 5 s (six pulses, 5 s each) at 20, 30, and 40 V, are shown in Figure 2.

For Al (110) surfaces, only highly ordered patterns of periodic stripes were observed for all voltages. Stripes covered the entire surface of the single crystal, i.e., a surface area of about 1 cm^2. At low voltages (20−30 V), two-dimensional dislocations were observed; with increased voltage, the dislocations almost disappeared, and at 40 V, they were observed only near point defects. The stripes were repeatedly found aligned along the $[\bar{1}10]$ direction, as determined by Laue X-ray diffractograms. The height of the stripes varied over the sample, in the range 1−7 nm. The periodicity of the stripes was 42 ± 2 nm at 20 V and 62 ± 2 nm at 30−50 V.

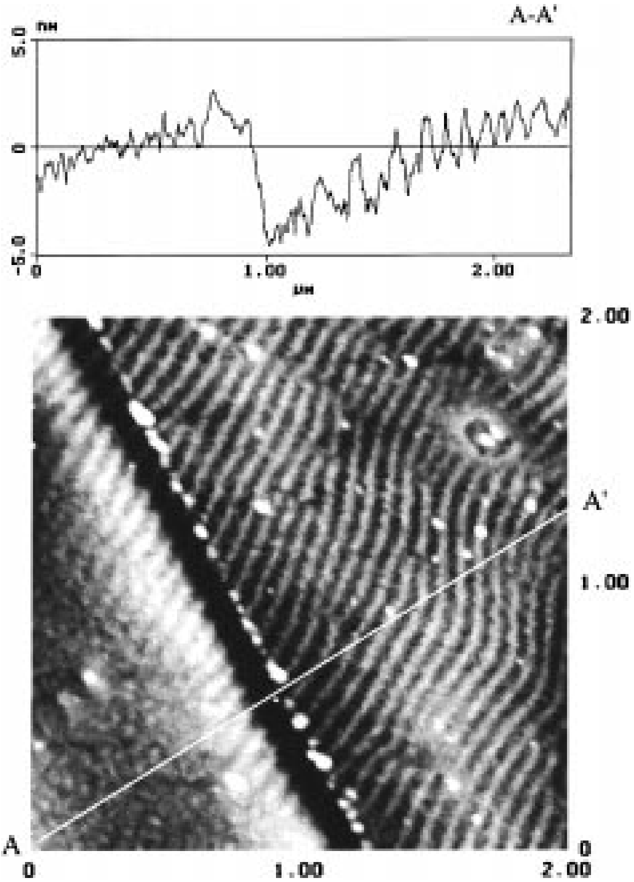

Figure 1. AFM image (scan size 2 × 2 μm) of polycrystalline Al electropolished at 40 V for 10 × 5 s near a grain boundary. Top: depth profile observed along the AA′ line.

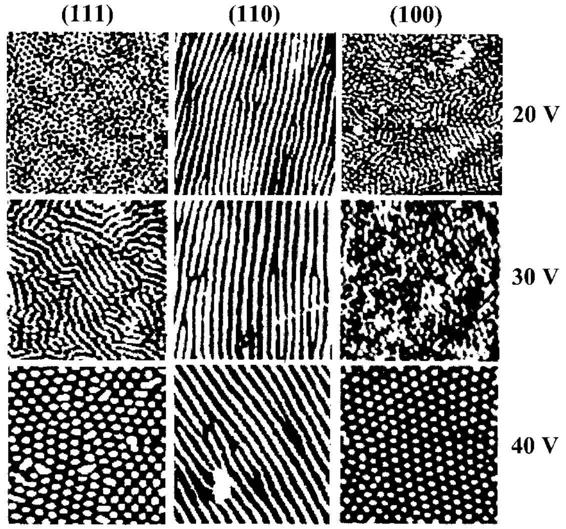

Figure 2. AFM images (1 × 1 μm) of Al single crystals produced by electropolishing for 6 × 5 s at 20, 30, and 40 V.

Electropolishing above 40 V produced deeper stripes (height 3−8 nm), but the quality of the sample deteriorated on the micrometer scale. Stripes were seen on Al(110) at lower voltages than those reported earlier on polycrystalline Al,[11−13] and they extended throughout the sample.

Under the same conditions, electropolished Al(100) or Al(111) surfaces did not exhibit regular stripes at any voltage. At 20 V, disordered structures for Al(100) and locally ordered small pits for Al(111) were obtained. At

30 V, disordered mounds and irregular short stripes were observed for Al(100) and Al(111). Above 35 V, quasiperiodic mounds (domain size 0.5−1 μm) with hexagonal order were obtained for both Al(100) and Al(111).

The conditions for forming stripes and hexagonal mounds on single crystals differ considerably from those found for polycrystalline Al.[11−13] The symmetries of (111), (100) and (110) faces of face-centered cubic Al are hexagonal, face-centered, and rectangular, respectively. The unilateral symmetry of stripes correlates with the rectangular symmetry of the Al(110) surface: rows of atoms 4.05 Å apart along [001], and 2.86 Å apart along the [$\bar{1}$10]. However, the interatomic distances are 2 orders of magnitude smaller than the observed topographic periodicity and thus cannot explain them.

The reported strong correlation between the length scale and symmetry of patterns and the applied voltage[11−13] suggested that an interfacial instability, caused by the preferential adsorption of alcohol molecules on surface ridges, may be responsible for pattern formation.[11−13] The variation in electropolishing patterns of Al single crystals may also be explained by a different adsorptivity of molecules on different crystalline faces.[15] Alternatively, mechanical stresses could drive self-ordering. Mechanical stresses, caused by heating−cooling cycles of the Al/Al_2O_3 interface, also produced periodic structures on a similar scale (100−210 nm).[4,5] A flat surface, stabilized by surface tension and by the preferential removal of ridges during electropolishing, is destabilized by stresses; disturbances of some wavelength will grow, whereas others will decay with time. These stresses may be caused by heating of the electrolyte/metal interface by the high electropolishing current (∼1 A cm^{-2}) or the diffusion of hydrogen into the metal, which has been observed in electropolished TiNi.[16] Hydrogen adsorption and incorporation into Al shows different features for different crystalline faces.[17]

In summary, we electropolished polycrystalline and monocrystalline samples of high purity Al and obtained well-defined nanoordered topographies, which were dependent on the surface crystalline orientation. The Al (110) surface exhibited a regular striped topography, extending over the whole sample (∼1 cm^2). The Al(111) and Al(100) surfaces showed only an ordered topography, with ridges at the positions of a hexagonal lattice, with 1 μm domains. We demonstrated that electropolishing can produce ordered topographies over dimensions of practical interest.

Acknowledgment. This work was supported by the U.S. Army Research Office (Grant DAA-H04-96-1-0316). We are grateful to Professor William D. Doyle for his interest and support.

CM990144G

---

(14) Landolt, D. *Electrochim. Acta* **1987**, *32*, 1.

(15) Trasatti, S.; Doubova, L. M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3311.

(16) Pound, B. G. *Acta Mater.* **1997**, *45*, 2059.

(17) Winkler, A.; Resch, C.; Rendulic, K. D. *J. Chem. Phys.* **1991**, *95*, 7682.