Two Dimensional Gold Nanodot Arrays Prepared by Using Self-Organized Nanostructure

Kyung-Han Jung*, Jeong-Soo Chang and Young-Soo Kwon†**

Abstract - Highly ordered gold nanodot arrays have been successfully obtained by vacuum evaporation using an anodic aluminum oxide (AAO) as a shadow mask. An AAO mask with the thickness of 300 nm was prepared through an anodization process. The structure of the nanodot arrays was studied by a field- emission scanning electron microscope (FE-SEM) equipped with an energy dispersive spectrometer (EDS). A tapping mode atomic force microscope (AFM) was employed for studies of height and phase feature. The nanodot arrays were precisely reproduced corresponding to the hexagonal structure of the AAO mask in a large area. In the gold nanodot arrays, the average diameter of dots is approximately the same as the AAO pore size in the range from 70 nm to 80 nm and 100 nm center-to-center spacing. EDS analysis indicated that the gold dots were almost entirely consisted of gold, a highly demanded material.

Keywords: anodic aluminum oxide, nanodot arrays, shadow mask, template vacuum evaporation

1. Introduction

Highly ordered nanodot arrays hold promise for many applications in various fields such as optical, magnetic, and electronic devices [1-3]. To date, various approaches have been explored in order to create these structures by using electron beam lithography, molecular beam epitaxy, scanning probe lithography, and template methods [4-6]. Among them, the research of template methods has increased rapidly due to its attractive potential use for the alternative approach to overcome the size scale limitation of conventional lithography with low cost [3, 7-9].

The anodic aluminum oxide (AAO), one of the promising templates, is a self organized nanoscale structure and consists of highly ordered hexagonal arrays of straight and parallel pores. Because the AAO grows under the anodization process, the pore size (20 ~200 nm) and the thickness (100 nm ~ tens ㎛) of the AAO are determined with controlling the anodic voltage and the type of electrolyte.

In this study, we attempted to make gold nanodot arrays, which were prepared using an AAO as an evaporation mask. A through-hole AAO was used for the preparation of gold nanodot arrays. The morphology of gold nanodot arrays was studied by using field-emission scanning electron microscopy (FE-SEM). Typical dimensions of gold nanodot arrays prepared by this work were 75 nm in diameter and 100 nm center-to-center spacing with 25 nm height. The diameter and spacing of the nanodot arrays corresponded to those of the AAO template. Energy dispersive spectrometer (EDS) analysis indicated that the gold nanodot arrays were almost consisted of pure gold.

† Corresponding Author: Dept. of Electrical Engineering, Dong-A University, Korea. (yskwon@dau.ac.kr)
* Dept. of Electrical Engineering, Dong-A University, Korea. (khjung@donga.ac.kr)
** School of Computer Control & Electrical Engineering, Kyungil University, Korea. (jsoo@kiu.ac.kr)
Received December 14, 2005 ; Accepted February 13, 2006

2. Experiment

2.1 Preparation of AAO mask

An AAO with the thickness of 300 nm was prepared via a two-step anodization process [10]. Firstly, a high purity aluminum sheet (Aldrich, 0.5 mm thick, 99.999%) was degreased in acetone and then annealed at 550°C for 15 min. to enhance its grain size and remove mechanical stresses. Subsequently, the aluminum sheet was mechanically polished with 6, 3, 1, and 0.25 ㎛ diamond suspension. The first anodization with this sample was carried out in a 0.3 M oxalic acid solution at 8°C under a constant voltage of 40 V for 2 h. The electrolyte was continuously stirred during the anodization to keep the temperature and concentration uniformity.

After the first anodization, the generated AAO was removed by wet chemical etching with a 60°C mixed solution of phosphoric acid (1.8 wt %) and chromic acid (2 wt %). Then the second anodization was carried out under the identical condition for 10 min.

After the second anodization, the surface of an AAO was covered with nail polish to avoid chemical damage during the chemical etching process. The remaining aluminum

substrate was removed by wet chemical etching with saturated $HgCl_2$ solution and then the barrier layer of the AAO was also removed with a 5 wt % H_3PO_4 solution at room temperature (RT). Finally, the nail polish protecting layer was removed in acetone and rinsed with ethanol and distilled water repeatedly before being bonded onto the substrate. The schematic illustation of the structure of an AAO is ideally drawn in Fig. 1 (a) and (b).

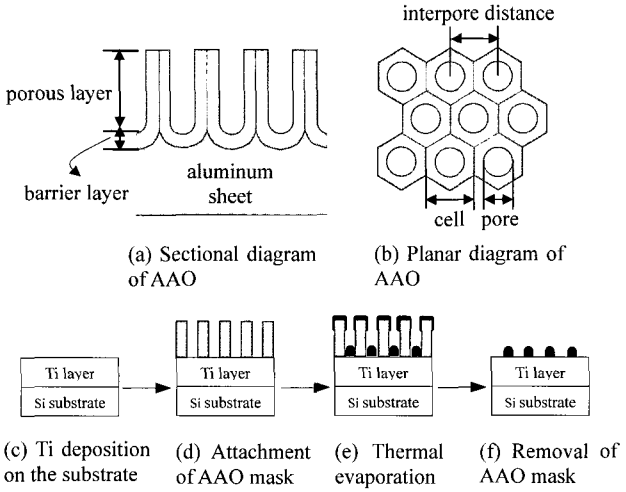

Fig. 1 Schematic illustrations of the ideal hexagonal structure of an AAO (a-b) and schematic diagrams of the fabrication of gold nanodot arrays (c-f). (a) The sectional diagram of an AAO. (b) The planar diagram of an AAO. (c) Ti film is deposited onto the substrate. (d) An AAO mask is set on the substrate. (e) Gold is deposited by thermal evaporation. (f) The mask is removed by chemical etching.

2.2 Gold dot arrays

The fabrication of gold nanodot arrays was carried out using the process schematically illustrated in Fig. 1 (c) through (f). A Ti thin film was first deposited on the substrate by thermal evaporation to enhance the adhesive strength between gold dots and the substrate. The AAO mask was then set onto the substrate. Then the pure gold was also thermally deposited in the vacuum pressure of 1×10^{-6} torr. After deposition, the AAO template was dissolved with a 10 wt% H_3PO_4 solution at 30℃ for 1 h and then the sample was rinsed with distilled water.

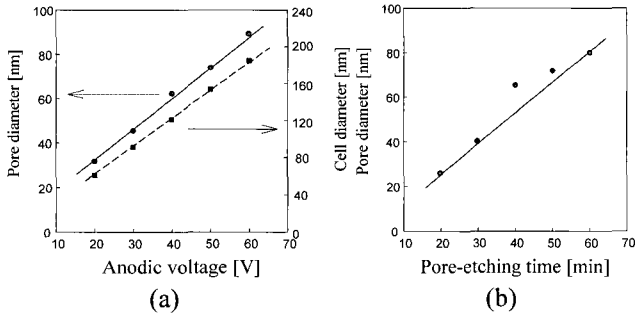

Fig. 2 (a) Average diameter of the pore and cell as a function of the anodic voltage. The oxalic acid concentration is 0.3 M and the temperature is 8°C. (b) Mean pore diameter with etching time.

2.3 Characterizations

The morphology of gold dot arrays was evaluated using a FE-SEM (JSM-6700F, JEOL) equipped with EDS (Oxford Instruments, INCA energy), which was performed to qualitatively examine elemental composition of the samples with a Mn Kα X-ray source ($h\nu$=136 eV). Atomic force microscopy (AFM, Nanoscope IIIa, Digital instruments) studies were performed for estimating the height or distance of the gold nanodot arrays with a tapping mode.

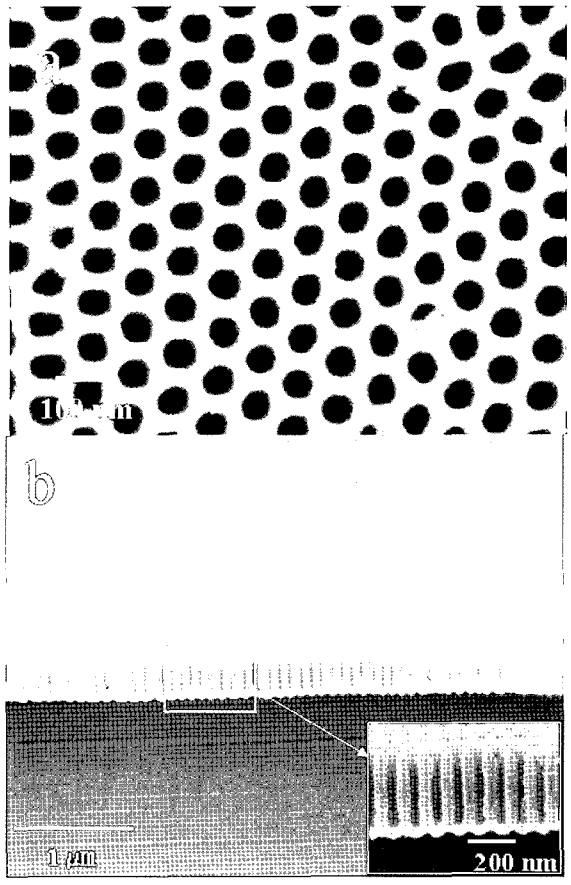

Fig. 3 FE-SEM images of an AAO mask. (a) Surface view. (b) Cross sectional view. The inset shows a close-up view of the hexagonal arrangement of the nanopores

The 10 μm scanner and cantilevers with force constants of 20-100 N/m at resonance frequencies of 260-280 kHz were used. Images included 512×512 data points.

3. Results and Discussion

The voltage dependence of the pore and cell diameters is shown in Fig. 2 (a). The pore and cell diameters proportionally increased with increasing voltage, as previously reported [11]. Fig. 2 (b) represents that the mean pore diameter is increased with etching time monotonously. This result shows that pore widening rate of our templates in a 5 wt % H_3PO_4 solution at RT is 1.4 nm/min approximately.

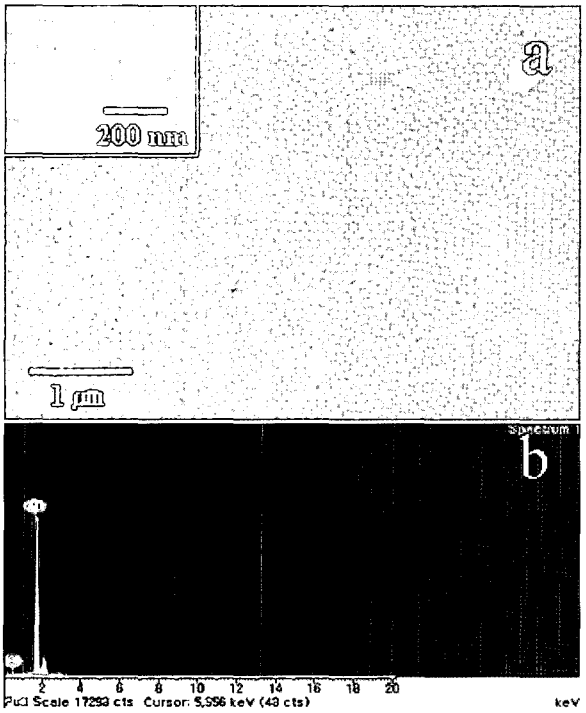

Fig. 4 (a) FE-SEM image of gold dot arrays. The inset shows a close-up view of the hexagonal arrangement of the nanodot arrays. (b) EDS spectrum revealing that the gold dot arrays are composed of highly demanded gold.

FE-SEM images of the planar and sectional views of the AAO prepared by two-step anodization are shown in Fig. 3 (a) and (b), respectively. The arrangement of pores is almost perfect hexagonal order and the average pore diameter is 65 nm. The interpore distance is about 100 nm corresponding to the cell diameter of AAO. To our knowledge, well-ordered nanopore arrays were formed when the root mean square (RMS) roughness of the aluminum sheet was less than 3 nm in 3×3 μm^2 as measured with an AFM after the polishing procedure. The pore density is $1 \times 10^{10}/cm^2$ [10]. The cross sectional view of AAO is presented in Fig. 3 (b). Pores are perpendicular to the substrate and parallel with each other. It is clearly shown that the bottoms of pores are blocked with a barrier layer (see inset). Therefore, the removal of the barrier layer is essential to achieve through-hole mask. The thickness of AAO plays an important role in the use of a shadow mask because evaporated vapor could not migrate to the substrate through the long nanopores. We recognized that scarcely any gold dot arrays were observed when the thickness of AAO exceeded 500 nm. Accordingly, we controlled the second anodization time in order to obtain thin AAO less than 500 nm.

Fig. 4 (a) shows the FE-SEM image of gold dot arrays produced on the substrate using an AAO as a shadow mask Highly ordered dot arrays are seen in a large area with the same hexagonal shape as that of the AAO mask.

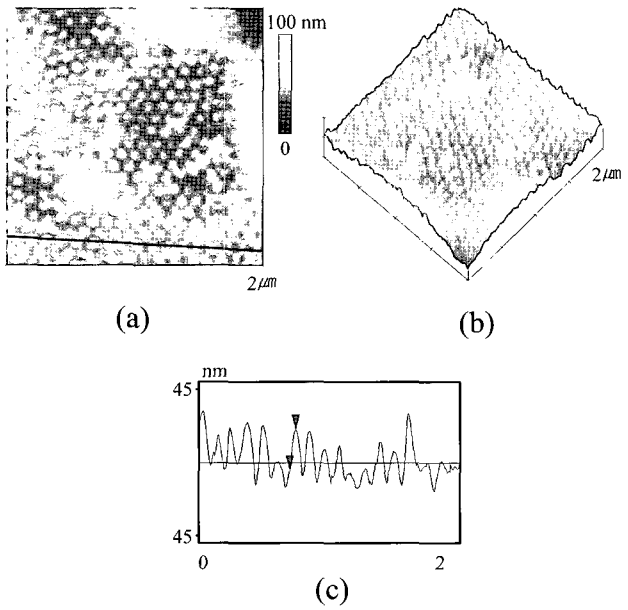

Fig. 5 AFM images of gold dot arrays. (a) Plane view, (b) phase view, and (c) cross sectional view along a line on (a).

The dots also maintain the same circular feature as the pores of the AAO mask with good size uniformity.These results indicate that gold dot arrays were well defined by the through-hole arrays of the AAO mask. The average diameter is about 75 nm, about 10 nm larger than that of the pore of the AAO mask in Fig. 3 (a) while keeping the lattice spacing constant at 100 nm, the same as that of the AAO mask. It is thought that the pore widening during the removing process of the barrier layer could induce the enhancement of the dot size. The high magnification view is shown in the inset. The EDS analysis in Fig. 4 (b) indicates that the dominant element is highly demanded gold.

Fig. 5 (a) and (b) illustrate an AFM plan view and phase view of the nanodot arrays, respectively. Bright parts correspond to the protruding dot arrays and dark parts indicate narrow gap between neighbouring dots. Distinct dot arrays with hemispherical-shape are clearly observed in

the phase view image shown in Fig. 5 (b). The average height of each dot is measured to be around 25 nm from the cross sectional analysis as shown in Fig. 5 (c). The period of the dot arrangement is about 100 nm, almost the same as that of the interpore distance of the AAO mask. The concave and convex topography of the dot arrays can also be clearly seen from cross sectional analysis.

4. Conclusion

Gold nanodot arrays were fabricated by using an AAO as a shadow mask. The characterization of the gold dot arrays was carried out by FE-SEM, EDS, and tapping mode AFM. The dimensions of the nanodot were 75 nm in diameter, 25 nm in thickness and 100 nm center-to-center spacing. The diameter, height, and spacing of the rings are dependent on those of the AAO mask. EDS analysis indicated that the gold dot arrays were almost entirely comprised of the highly demanded gold in the arrays. The present technique is expected to applicant easily for the development of nanoscale devices.

Acknowledgements

This work was supported by the MOCIE through the CIIPMS at Dong-A University.

References

[1] R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W.J. Mahoney and R.G. Osifchin, "Self-assembly of a two-dimensional superlattice of molecularly linked metal clusters", *Science*, vol. 203, pp. 1690-1693, 1996.

[2] (a) Y.S. Choi, Y.S. Kwon, E. Tamiya, D.H. Park, "Three-dimensional self-assembled micro-array using magnetic force", *KIEE Int. Trans. on EA*, vol.3-C, pp. 182-188, 2003, (b) D. Routkevitch, A.A. Tager, J. Haruyama, D. Almawlawi, M. Moskovits and J.M. Xu, "Nonlithographic nano-wire arrays: Fabrication, physics, and device applications", *IEEE Trans. Elec. Dev.*, vol. 43, pp. 1646-1658, 1996.

[3] (a) H.J. Kim, P. Kalappa, W.K. Son, J.E.Park, T. Oshaka, H.H. Kim, J.S. Hong and S.G. Park, "Preparation and characterization of TiO_2 filled sulfonated poly (ether ether ketone) nanocomposite membranes for direct methanol fuel cells", *KIEE Int. Trans. on EA*, vol. 5-C, pp. 165-170, 2005, (b) K. Liu, J. Nogués, C. Leighton, H. Masuda, K. Nishio, I.V. Roshchin and I.K. Schuller, "Fabrication and thermal stability of arrays of Fe nanodots", *Appl. Phys. Lett.* vol. 81, pp. 4434-4436, 2002.

[4] T. Aoyama, K. Uchiyama, T. Kagotani, K. Hattori, Y. Wada, S. Okawa, H. Hatate, H. Nishio and I. Sato, "Fabrication and properties of CoPt patterned media with perpendicular magnetic anisotropy", *IEEE Trans. Mag.*, vol. 37, pp. 1646-1648, 2001.

[5] P. Vavassori, O. Donzelli, L. Callegaro, M. Grimsditch and V. Metlushko, "Magnetic domain structure and magnetic reversal in elliptical dot arrays", *IEEE Trans. Mag.*, vol. 36, pp. 2993-2995, 2000.

[6] Y. B. Xu, A. Hirohata, S. M. Gardiner, M. Tselepi, J. Rothman, M. Kläui, L. Lopez-Diaz, J. A. C. Bland, Y. Chen, E. Cambril and F. Rousseaux, "Effects of Interdot Dipole Coupling in Mesoscopic Epitaxial Fe(100) Dot Arrays", *IEEE Trans. Mag.*, vol. 37, pp. 2055-2057, 2001.

[7] K.H. Jung, J.W. Yoon, N. Koshizaki and Y.S. Kwon, "Fabrication of gold dot and tubular gold arrays using anodic aluminum oxide film as template", *Jpn. J. Appl. Phys.*, vol. 44, pp. 5300-5303, 2005.

[8] K. Nielsch, R. Hertel, R.B. Wehrspohn, J. Barthel, J. Kirschner, U. Gösele, S.F. Fischer and H. Kronmüller, "Switching behavior of single nanowires inside dense nickel nanowire arrays", *IEEE Trans. Mag.*, vol. 38, pp. 2571-2573, 2002.

[9] W.B. Choi, E. Bae, D. Kang, S. Chae, B.H. Cheong, J. Ko, E. Lee and W. Park, "Aligned carbon nanotubes for nanoelectronics", *Nanotechnology*, vol. 15, pp. S512-S516, 2004.

[10] K.H. Jung, H.K. Shin and Y.S. Kwon, "A study of nanoscale structure of anodic porous alumina film", *J. of KIEEME*, vol. 16, pp. 801-806, 2003.

[11] X. Wang and G.R. Han, "Fabrication and characterization of anodic aluminum oxide template", *Microelectron. Eng.*, vol. 66, pp. 166-170, 2003.

Kyung-Han Jung

He was born in Busan, Korea in 1972. He received his B.S. and M.S. degrees in Physics from Dong-A University in 2000 and 2002, respectively. He is currently a Ph.D. candidate in Electrical Engineering at the same Institution. His main research interests are in the areas of molecular electronics, nanostructured materials, and SPM and its applications.

Jeong-Soo Chang

He was born in Seoul, Korea, in 1943. He received his B.S., M.S. and Ph.D. degree in Electrical Engineering from Yeungnam University in 1974, 1980 and 1995, respectively. Now, he is a professor at the School of Computer Control & Electrical Engineering, Kyungil University. His main research interests are in the areas of electric power & material, organic thin films and its applications.

Young-Soo Kwon

He was born in Andong, Korea in 1950. He received his B.S. degree in Electrical Engineering from Yeoungnam University, his M.S. degree in Electrical Engineering from Kyoungpook National University and his Ph.D. degree in Molecular Devices from the Tokyo Institute of Technology in 1972, 1976 and 1988, respectively. Now, he is a Professor in the Department of Electrical Engineering at Dong-A University, Korea. His main research interests are in the areas of molecular electronics, and ultra-thin films and their applications.