

Fabrication of Highly Ordered Gold Nanorods Film Using Alumina Nanopores

Z. Soltani^{a,*}, M. Moradi^b, M. Noormohammadi^b, F. Behzadi^b

^a *Department of Physics, Shiraz Branch, Islamic Azad University, Shiraz, Iran*

^b *Department of Physics, Shiraz University, P. O. Box 71454 Shiraz, Iran*

Article history:

Received 2/6/2012

Accepted 19/8/2012

Published online 1/9/2012

Keywords:

Porous anodic alumina

Thermal evaporation

Gold nanorod

Nanopores

**Corresponding author:*

E-mail address:

zsoltany@yahoo.com

Phone: +98 711 2358441

Fax: +98 711 2358441

Abstract

A simple method for fabrication of highly ordered gold nanorod film is introduced in this article. The procedure is based on thermal evaporation of gold into a porous anodic alumina film (PAA). The PPA film was fabricated by combining the hard and mild anodization. This combination effectively decreases the processing time of fabrication of highly ordered porous anodic alumina film with controlled pore diameter and length. It was found that gold nanorods configuration affected by the porous anodic alumina film structure such as pore diameter and length. Furthermore the evaporation process change the rods diameter along the nanopores via the decreasing the pore mouth during the gold deposition.

2012 JNS All rights reserved

1. Introduction

Dense arrays of nanometer scale structure such as nanodots, nanorods and nanowires have considerable applications in nanometric device fabrication. Among these nanostructures, gold nanodots and nanorods exhibit localized surface plasmon resonance and surface enhanced Raman scattering properties [1-3]. Recent works have shown a great potential of gold nanostructures

applications in the field of optoelectronics [4-5], sensors [6-7] and catalysis [8]. Several methods have been used to fabricate the material nanostructures such as various lithographic techniques [9-10], deposition into ordered template [11], self assembly [12] and selective etching [13]. Although lithographic techniques allow us to control the size and shape of gold nanostructures, these techniques are expensive. Template methods

are generally inexpensive in comparison to lithographic techniques and allow depositing the wide range of materials. Among templates, porous anodic alumina (PAA) has been one of the most popular templates to fabricate a variety of nanostructure materials. PAA film has a well-ordered array of straight pore obtained by mild anodization (MA) [14-16] and hard Anodization (HA) [17-18]. MA in comparison with HA, is a slow process and limited to special growth regimes. HA considerably speeds up the anodization process and it is applicable to fabricate the ordered PAA in various range pore size and interpore distances. Since the mouth of the pores is blocked during the deposition by the common deposition techniques like ion sputtering or thermal evaporation, there is a limitation to produce controllable long nanorod inside the pores. In this paper, we report the fabrication of ordered gold nanorod arrays by thermal deposition of gold into a PAA film fabricated via two steps: HA and MA Process. It is also shown how the blocking of the tops of pores during the gold deposition can be controlled by attention to the depth and diameter of the pores.

2. Experimental

A high purity (99.999%) aluminum foil, 0.5 mm of thickness and 1.2 cm of diameter, was degreased in acetone and washed by deionized water. The sample was then electropolished in a 1:4 volume mixture of HClO₄ and C₂H₅OH at a constant current density of 100 mA/cm² for 3 min to reduce the roughness of aluminum sample. To obtain the highly ordered pores with interpore distance 260 nm and different depth, a two-steps HA and MA process was employed. In this interpore distance (260nm), fabrication of PAA film with highly ordered pores is impossible directly by MA process and it is needed to be pre-patterned [16]. In HA

process at first the protective layer was created at 40V for ten minutes to avoid sample from burning at high voltage in HA [18]. The anodization voltage then increased to a final value 130 V, and kept constant for 1h.

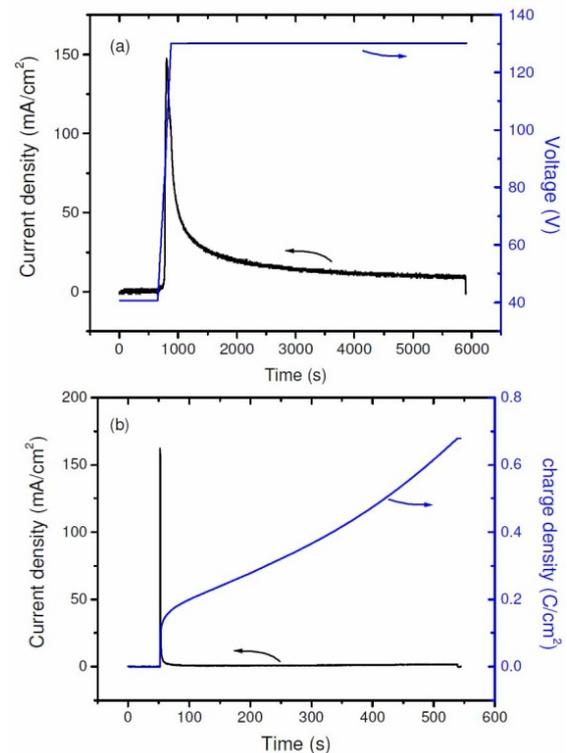


Fig. 1. Current density and charge density versus time during (a) hard anodization and (b) conventional mild anodization process.

To keep the sample at 0 °C the multi-channel electrochemical cell was designed to HA process. The alumina layer formed in HA was removed by wet chemical etching using a mixture of 0.5 molar (M) phosphoric acid and 0.2 M chromic acid. The second step MA process was done at voltage 104 V and temperature 3 °C. This MA voltage was chosen based on the linear relation between interpore distance and the anodization voltage. It is considerable that the interpore distance obtained from HA process

should be the same as the MA process. As shown in Fig 1a, in HA process, the anodization current density increased when the voltage increased, and after that it decreased slowly. But, during the MA process of second step anodization (Fig. 1b), current behavior is the same as the conventional MA. Then the pore diameter becomes wider by using 0.5 M acid phosphoric in 30 °C. After that gold was deposited into the PAA film by thermal evaporation in low pressure (10^{-5} Torr). The evaporation rate was about 0.3 nm/s and controlled by quartz crystal during the deposition. To release the gold nanorods, the coated gold face was glued by gum. The PAA film was removed from gold film by chemical dissolution using 1 M sodium hydroxide at room temperature to get nanorod Arrays. The PAA film and gold nanorod were characterized by scanning electron microscopy (SEM).

3. Results and discussion

As it is shown in Fig. 2, the pore arrangement shows the high degree of pore ordering obtained by the HA process. Therefore one of the HA advantages is its ability to fabricate a highly ordered PAA film in a short time (about 1h) due to high speed film growth rate. The MA process is carried out as the second step. The ordered hexagonal pattern formed in HA process, preserves after the second step (MA), Fig. 2.

In MA Process it is possible to control the pore depth, L_p , by measuring the transferred charge, Q , during the anodization. It was shown [19] that the pore depth is linearly proportional to the transferred charge density during each time interval. Two different pore depth of the PAA films correspond to different Q are presented in Fig. 3.

The diameter is controllably increased by chemical etching and the rate of alumina dissolution in 0.5 M phosphoric acid at 30 °C is about 0.025 nm/s [20].

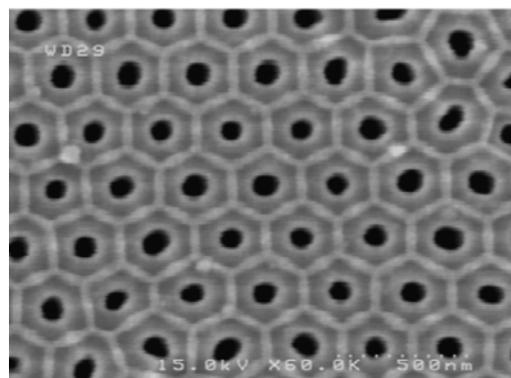


Fig. 2. The SEM micrograph image of nanopore configuration of sample made in the oxalic acid 0.3 M at 130 V anodization voltage.

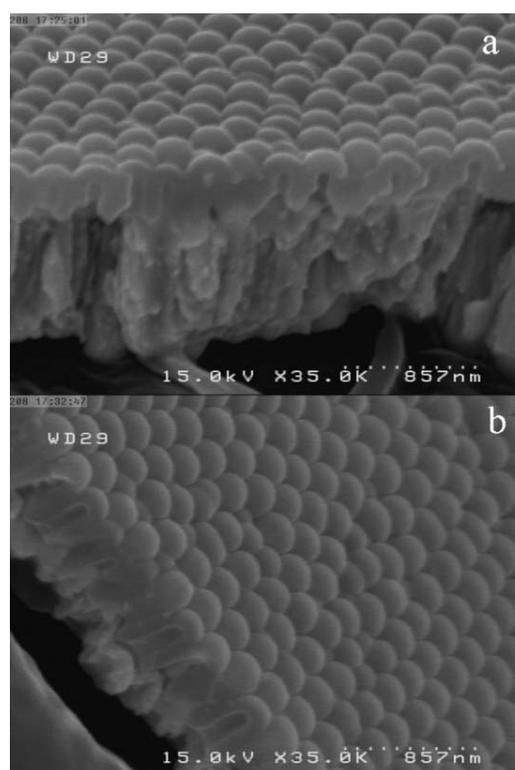


Fig. 3. The cross section SEM micrographs of nanopore configurations of samples (MA process) made in phosphoric/oxalic acid mixture containing 0.05 M oxalic and 0.02 M phosphoric acid at the anodization voltage, 104 V by different pore depth.

Of course without chemical etching, the tops of pores are blocking quickly during thermal evaporation, and the nanorod formation inside the pores will be stopped. Therefore it is necessary to widen the pores by chemical solution in phosphoric acid about 50 min. This process increases the pore diameter from 80 nm to 240 nm as it is shown in Fig. 4.

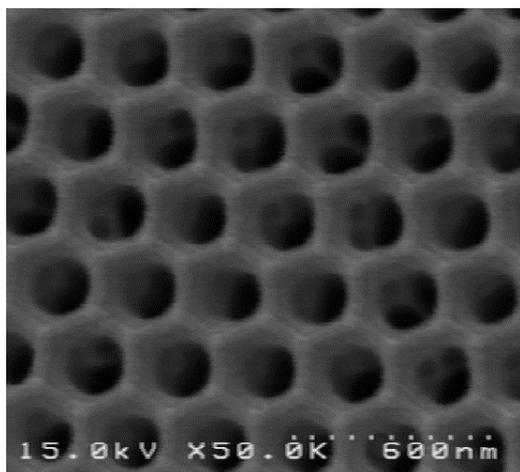


Fig. 4. The SEM micrograph image of nanopore when pore widening was carried out for 50 min in 0.5 M phosphoric acid (H_3PO_4) at $30^\circ C$.

In this stage, the template is ready for thermal evaporation of gold. In contrast to other deposition techniques (e.g., sputtering), the evaporating gold produced by thermal evaporation has a long mean free path due to the low pressure in the chamber ($<10^{-6}$ Torr); thus, it is approximately collimated after traveling from the source to the PAA film substrate (15 cm total distance).

The SEM images of the gold nanorods after the chemical removing of the PAA film for two different lengths are shown in Fig. 5, 6. These images show an array of free-standing, parallel rods which are located on gold substance.

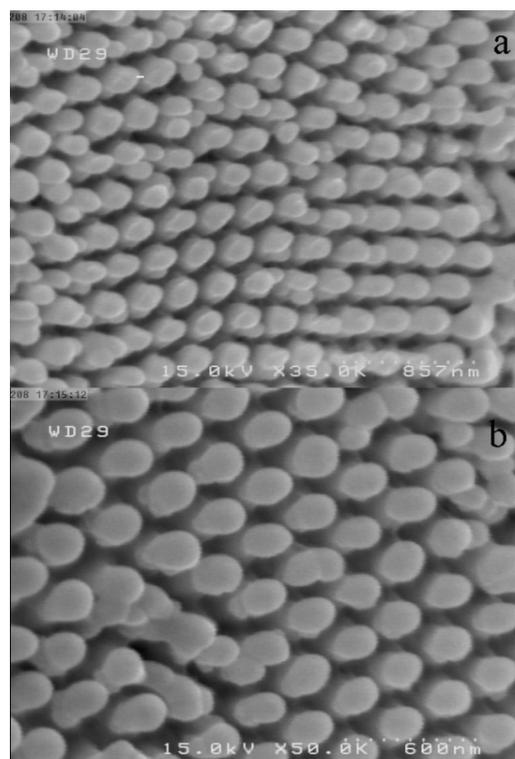


Fig. 5. SEM images of the gold nanorods arrays prepared within a PAA template with 350 nm pore length: (a) low and (b) high magnification.

The tip of the rods produced at the bottom of the pores has a diameter larger than that of the other parts. Because at the beginning of deposition, the pore mouth has the largest diameter, therefore the evaporated gold reaches to the bottom of the pore in largest area, but by passing time, the diameter of the pore mouth decreases because of the deposition of the evaporated gold on the surface around the pore mouth. Furthermore the end of nanorods produced at the tops of pores has a lower diameter, as it is shown in Figs. 5 and 6, this event for long nanorods is more effective. After removing the PAA, the direction of nanorods with smaller length remains straight (Fig. 5) but the long nanorods bend such that the tips of these rods connect to each other (Fig. 6).

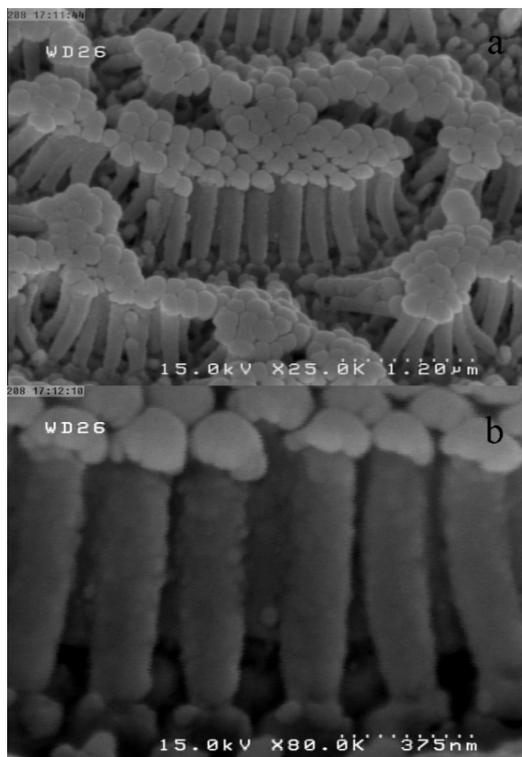


Fig. 6. SEM images of the gold nanorods arrays prepared within a PAA template with 850 nm pore length: (a) low and (b) high magnification.

4. Conclusion

The results of this study demonstrate the arrays of ordered gold nanorods fabricated by thermal evaporation into a PAA template. PAA film was fabricated via two step HA and MA Process in short processing time. The SEM analyze was shown that the ordered hexagonal pattern formed in HA process, transfer to the PAA film obtained after second step (MA).

The effects of pore depth and diameter on the nanorods formation were investigated and the following conclusions have been achieved:

1. Low diameter of pore leads to block the tops of pores quickly during thermal evaporation and the solution for this problem is widening of pores more than 150nm.

2. The tips of the rods have a larger diameter relative to other parts because of the gold deposition on the tops of pores and made the narrow space to transfere particles into them.

3. The direction of the nanorods depends on their lengths. Longer nanorods bend to each other but the smaller ones are straight.

Acknowledgements

This work was supported by Shiraz Islamic Azad University as a research project.

References

- [1] Z. S. Li, C. X. Kan and W. P. Cai, *Appl. Phys. Lett.* 82 (2003) 1392.
- [2] F. Matsumoto, M. Ishikawa, K. Nishio and H. Masuda, *Chem. Lett.* 34 (2005) 508.
- [3] M. D. Dickey, E. A. Weiss, E. J. Smythe, R. C. Chiechi, F. Capasso, and G. M. Whitesides, *ACS Nano* 2 (2008) 800-808.
- [4] S. H. Lim, W. Mar, P. Matheu, D. Derkacs and E. T. Yu, *J. Appl. Phys.* 101 (2007) 104309.
- [5] M. K. Kwon, J. Y. Kim, B. H. Kim, I. K. Park, C. Y. Cho, C. C. Byeon and S. J. Park, *Adv. Mater.* 20 (2008) 1253.
- [6] K. Aslan, J. R. Lakowicz and C. D. Geddes, *Curr. Opin. Chem. Biol.* 9 (2005) 538.
- [7] H. Haick, *J. Phys. D: Appl. Phys.* 40 (2007) 7173.
- [8] M. S. El-Deab and T. Ohsaka, *Electrochem. Commun.* 4 (2002) 288.
- [9] G. M. Wallraff, W. D. Hinsberg, *Chem. Rev.* 99 (7) (1999) 1801-1821.
- [10] R. M. Nyffenegger and R. M. Penner, *Chem. Rev.* 97 (1997) 1195.
- [11] J. Viernow, D. Y. Petrivykh, E. K. Men, A. Kirakosian, J. L. Lin and E. J. Himpsel, *Appl. Phys. Lett.* 74 (1999) 2125.
- [12] B. G. Prevo, J. C. Fuller and O. D. Velev,

- Chem. Mater. 17 (2005) 28.
- [13] F. K. Liu, Y.C. Chang, F. H. Ko, T. C. Chu and B. T. Dai, *Microelectron. Eng.* 67/68 (2003) 702.
- [14] O. Jessensky, F. Muller and U. Gosele, *J. Electrochem. Soc.* 145 (1998) 3735.
- [15] H. Masuda and K. Fukuda, *Science* 268 (1995) 1466.
- [16] K. Nielsch, J. Choi, K. Schwirn, R. B. Wehrspohn and U. Gosele, *Nano Lett.* 2 (2002) 677.
- [17] S. Z. Chu, K. Wada, S. Inoue, M. Isogai and A. Yasumori, *Adv. Mater.* 172 (2005) 115.
- [18] W. Lee, R. Ji, U. Gosele and K. Nielsch, *Nature Mater.* 5 (2006) 741.
- [19] M. Moradi, M. Noormohammadi, F. Behzadi, *J. Phys. D: Appl. Phys.* 44 (2011) 045301.
- [20] M. Lillo and D. Losic, *Journal of Membrane Science* 327 (2009) 11–17.