Realization of vertically aligned 1-D Ferrous nanorods using template assisted electrochemical deposition

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Abstract. In this work, we report on the synthesis of vertically aligned ferrous (Fe) nanorods using aluminium oxide template (AAO). Initially, a thick layer of gold was deposited on one side of the anodic aluminium oxide template to realize a good electrically conductive surface. The other side of the AAO is subjected to pore widening technique using phosphoric acid before electrochemically depositing Fe inside the pores. After deposition, the template was removed and the resulting free-standing Fe nanorods were found to have grown along the 110 plane. We controlled the dimensions of the Fe nanorods by varying parameters such as the concentration of electrolyte solution and the rate of electrodeposition. This growth technique is advantageous since there is uniformity in the sizes of nanorods and the free-standing nanorods provides an ideal platform for making Fe nanorod based memories.

1. Introduction

Low dimensional structures exhibit interesting physical properties compared to that of their bulk counterparts due to quantum confinement effect. Reducing dimensions from 3D to 0D drastically modifies the electron density of states which in turn affect the electrical, optical and structural properties of the material [1-3]. By exerting suitable control over the dimension of the materials one can tailor the properties of the materials which will find applications in electronics, biomedical sciences, optics, magnetism and energy storage. There are different techniques to synthesize low dimensional structures using bottom-up approach such as physical vapour deposition, chemical vapour deposition, self-assembly, sol-gel and electrodeposition techniques [4]. Of all these techniques, electrodeposition is the most efficient technique for manipulating the texture, morphology and size of materials [3]. It is possible to synthesize a wide range of nanostructures such as nanotubes, nanowires and nanobelts by controlling the reaction rate and chemical constituents. Another advantage is that it is possible to fabricate large scale and highly oriented nanorods on any conductive or non-conductive substrate. This method is widely used in comparison to other methods since growing nanostructures using this technique is simpler and offers the advantage of easy scalability [5].

The electrodeposition technique is a three-electrode electrochemical cell which uses both galvanostatic and potentiostatic technique for deposition [6]. In the former method, a constant current is maintained between the two electrodes (such as working and counter electrode) and the voltage is measured between the working and reference electrode [7]. On the other hand, in the potentiostatic deposition, a constant voltage is applied between the working and counter electrode and the variation
in current as a function of time is measured. The advantage of using the potentiostatic mode is that, in a mixture of solution, one can aim for a particular reaction or product since the deposition potential for each material will be different. For instance, in an electrolyte containing ferrous sulphate and copper sulphate solution, it is possible to deposit ferrous and copper sequentially by using appropriate deposition potential. After completing the deposition process, one can easily remove the template to realize free standing nanorods. The surface morphology of the electrodeposited materials relies on the chemical composition of the electrode surface and the electrochemical parameters [8]. In this work, we report the synthesis of an ordered array of ferrous nanorods using template assisted electrodeposition and investigate their material properties [8,9].

Growing nanostructures using electrochemical technique involves depositing the desired material onto a nanoporous anodized alumina oxide (AAO) template [10]. The material is deposited by applying suitable deposition potential to the gold-coated AAO template and the magnitude of the potential determines the rate of deposition of material in the AAO membrane. By changing the deposition potential it is possible to gain control over the diameter and length of the nanorods. This technique can also be used to grow multi-junction nanorods by carrying out multiple depositions on the same AAO template using different electrolytic solution. Ordered arrays of metals (Fe, Ni, Ag) and semiconductor (ZnO, CdSe) can be easily grown using this technique [10]. Such ordered arrays of nanorods on a conductive substrate with controllable configuration and structure have potential applications in luminescent diodes, magnetic recording devices, solar cells, sensors and nanowire or nanorods based electrical devices [11-13].

It is also important to note that the physical properties of the nanorods does not rely only on the size but also on their orientation [11]. Though many works have been done to grow metallic nanorods, the realization of highly ordered arrays of nanomaterials is difficult [13]. The difficulty lies in precisely controlling the simultaneous growth of nanorods without making physical contact with each other is highly challenging. Therefore it will be highly advantageous to establish a simple growth recipe for obtaining ordered arrays of nanorods with good size distribution and shape using AAO template. One of the challenge in using AAO template for nanorod synthesis is the removal of template after the deposition process. Etching rate of AAO template varies significantly depending upon the type of material embedded in the pores of the template [14]. Another problem while etching is that the procedure inadvertently damages the active material inside the pores. So one has to be careful in choosing the type of etchant and etching parameters for successful realization of vertically aligned nanorods [15-16]. In this work we had established experimental protocol for synthesizing vertically aligned Ferrous nanorods as there are scarcely any reports on the growth of ferrous nanorods by this method. Our synthesize technique can also be extended to any obtain vertically aligned nanorods of any other ferromagnetic materials.

2. Materials and Methods

AAO template with an average pore size of 100 nm is chosen for growing Fe nanorods [2,17]. Initially, the template was subjected to the cleansing process using acetone and ethanol by ultrasonication followed by washing it with copious amount of water. Then the template was coated with thermally evaporated gold to serve as a conductive surface and also to act as a working electrode in the electro chemical cell. Platinum wire is used as a counter electrode with a small glass tube containing Ag/AgCl solution acting as the reference electrode. The electrolyte solution used for the synthesis of 1 D Fe nanorods was prepared by mixing Ferrous sulphate (FeSO\(_4\cdot7\)H\(_2\)O) solution, Boric acid (H\(_3\)BO\(_3\)), Ascorbic acid (C\(_6\)H\(_7\)O\(_6\)) and Sulfamic acid [16]. Each solution was prepared separately and then mixed in a 100 ml beaker. The total volume of the solution is 40 ml and maintained at a PH value of 4. Before carrying out electrodeposition on the AAO template linear sweep voltammetry was performed to determine the deposition potential. This deposition potential was then used to deposit Fe
inside the pores of the AAO template using the chronoamperometric technique. Multiple deposition (3 to 4) cycles each spanning about 10 mts duration were done to completely fill the pores of the AAO template. After electrodeposition, AAO template was dissolved using sodium hydroxide solution to get the free-standing nanorods.

3. Results and Discussion

At first the commercially obtained AAO template is subjected to pore widening technique. This method modifies the diameter of the pores of the template affecting the pore density. The pore widening technique plays a key role in enhancing the uniformity of hexagonally arranged pores. It also improves the nucleation of metals inside the template by allowing easy penetration of the electrolyte solution during the electrodeposition process. AAO templates shown in ‘figure 1 (a)’ with a mean pore size of 100 nm was subjected to pore widening prior to Au evaporation. This was done by soaking the templates for about 30 mts in 5 wt% of phosphoric acid which serves as a mild etching solution [7]. This helped in widening the pores of AAO templates to 270-310 nm as shown in the ‘figure 1(b)’. The extended pores allows smooth and easy deposition of metals and promote homogeneous growth of nanorods [19,20].

![Figure 1](image-url)

Figure 1. SEM image of (a) AAO template before pore widening (b) AAO template after pore widening

One side of the pore widened template is then coated with 300nm of gold as an adhesion layer to provide the conductive base for the electrodeposition to take place. This Au sputtered template was then used as a working electrode along with Platinum wire as the counter electrode, Ag/AgCl electrode as the reference electrode in a three electrode system. In ‘figure 2’ it is seen that the sputtered gold has entered into the pores through the side walls of the template. This facilitates a conductive support for the growth of nanorods that are electrochemically deposited.
Using the desired electrolyte solution and the potential of -1.2V found from the linear sweep voltammetric technique, ferrous was deposited into the pores of the AAO template [18]. The growth of the species is a bottom–up–growing process [2]. The deposition initially starts from the the pore walls followed by gradual deposition build up inwardly towards the center [5]. To confirm the presence of the nanorods the samples were viewed under the scanning electron microscope. ‘Figure 3(a)’ shows the SEM image of the pore widened AAO template with ferrous being electrochemically deposited. Though it is not completely filled and uniform it is seen that the solution has entered through the side walls of the pores that has gone deep inside the template. To confirm the existence of ferrous inside the pores the Energy-dispersive X-ray spectrum was done as seen in ‘figure 3(b)’. It shows that the obtained nanorods is free from impurities. The gold is present that comes from the thin layer of coating done using thermal evaporation and Al and O is the composition of the template used. This helped in realization that the tip of Fe nanorods do not show its presence at the top and are buried inside and no ferrous was deposited on the surface. And inorder to increase the length of the rods the deposition cycle vs time is tailored.

**Figure 2.** Top view of AAO template after Au sputtering

**Figure 3.** SEM image of (a) Top view of AAO with Fe deposited  (b) EDX spectrum of AAO template
The structure of the ferrous material deposited was studied using X-ray diffraction. This was done to ensure that the patterns formed due to the filled pores of the AAO template are of the species deposited. The X-ray pattern with the peaks corresponding to (110), (200) and (211) planes was obtained that were associated to Fe indicating a body centered structure with (110) orientation [16].

To obtain free-standing nanorods [21] and to check the nature of the ferrous nanorods inside the pores, the AAO template was completely dissolved into 0.5M of sodium hydroxide solution and centrifuged [14]. Since ferrous being magnetic in nature the resultant product was obtained by magnetic separation using a small bar magnet. This method helped to disarticulate the ferrous from alumina that was embedded inside the pores and result in pure ferrous nanorods. This was confirmed by taking the SEM image by dispersing the solution on the silicon substrate. ‘Figure 5’ shows the schematic separation of ferrous using the magnet from which the AAO template on its complete disintegration dissolves in the etchant and the ferrous gets attracted towards the magnet.
‘Figure 6’ shows the SEM image of ferrous nanorods that were magnetically separated and placed onto the silicon substrate. It is seen that the nanorods are of smaller in length. The length of the nanorods was made longer by increasing the number of deposition cycles. [22]. This helped in achieving Ferrous nanorods with longer length to width ratio. ‘Figure 7 (a) and 7(b)’ are the cross-sectional view of the AAO template. The pores of the template were filled to the larger extent that proportionally increased the yield of the ferrous nanorods. The template was then etched and magnetically separated as shown in ‘figure 7 (c) and (d)’.

Figure 6. SEM image of ferrous nanorods that are magnetically separated

Figure 7. (a) and (b) Cross sectional image of ferrous nanorods, (c) and (d) Ferrous nanorods that are magnetically separated
4. Conclusion

In summary, we have shown that the electrochemical deposition technique can be successfully used to synthesize 1-D ferrous nanorods. The commercially purchased AAO template was subjected to pore widening which facilitated easier penetration of deposition of ferrous inside the template. The ferrous was then electrochemically deposited inside the pores and then the template was removed to obtain free-standing array of rods. This was achieved by using the NaOH etchant solution by completely dissolving the template and magnetically separated to result in free-standing nanorods. The length of the nanorods was controlled by changing the deposition duration cycle. The samples showed a very good yield on magnetic separation from the AAO template.

5. References

[1] Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, Yin Y, Kim F and Yan H 2003 Advanced materials 15(5) pp.353-389
[2] Ali G, Ahmad M, Akhter J I, Maaz K, Karim S, Maqbool M and Yang S G, 2010 IEEE Transactions on Nanotechnology 9(2) pp 223-228
[3] Peng Y, Zhang H L, Pan S L and Li H L 2000 Journal of Applied Physics 87(10) pp 7405-7408
[4] Burda C, Chen X, Narayanan R, Ei-Sayed M A, Chem Rev 2005 105 1025
[5] Cao G and Liu D 2008 Advances in colloid and interface science 136(1-2) pp 45-64
[6] Mohl M, Kumar A, Reddy A L M, Kukovecz A, Konya Z, Kiricsi I, Vajtai R and Ajayan P M, 2009 The Journal of Physical Chemistry C 114(1) pp 389-393
[7] Yin A J, Li J, Jian W, Bennett A J and Xu J M 2001 Applied Physics Letters 79(7) pp 1039-1041
[8] Baik J M, Schierhorn M and Moskovits M, 2008 The Journal of Physical Chemistry C 112(7) pp 2252-2255
[9] Mao A, Han G Y and Park J H 2010 Journal of Materials Chemistry 20(11) pp 2247-2250
[10] Hu G, Zhang H, Di W and Zhao T, 2009 Applied Physics Research 1(2) p 78
[11] Cao H, Wang L, Qiu Y and Zhang L, 2006 Nanotechnology 17(6) p 1736
[12] Huang X, Li L, Luo X, Zhu X and Li G, 2008 The Journal of Physical Chemistry C 112(5) pp 1468-1472
[13] Gao T, Meng G, Wang Y, Sun S and Zhang L, 2001 Journal of Physics Condensed Matter 14(3) p 355
[14] Mohanty U S 2011 Journal of applied electrochemistry 41(3) pp 257-270
[15] Fert A and Piraux L 1999 Journal of Magnetism and Magnetic Materials 200(1-3) pp 338-358
[16] Guojun S O N G, Dong C H E N, Zhi P E N G, Xilin S H E, Jianjiang L I and Ping H A N 2009 Journal of Material Science and Technology 23(03) pp 427-429
[17] Lim J H, Chae W S, Lee H O, Malkinski L, Min S G, Wiley J B, Jun J H, Lee S H and Jung J S, 2010 Journal of Applied Physics 107(9) p 09A334
[18] Jee S E, Lee P S, Yoon B J, Jeong S H and Lee K H Chemistry of materials 17(16) pp 4049-4052
[19] Zhang J, Kielbasa J E and Carroll D L, 2010 Materials Chemistry and Physics 122(1) pp 295-300
[20] Zhao S, Roberge H, Yelon A and Veres T, 2006 Journal of the American Chemical Society 128(38) pp 12352-12353
[21] Fang D, Huang K, Liu S and Qin D, 2009 Electrochemistry Communications 11(4) pp 901-904
[22] Sadeghpour Motlagh M, Mokhtari Zonouzi K, Aghajani H and Kakroudi M G, 2014 Journal of Materials Engineering and Performance 23(6) pp 2007-2014
Acknowledgment
R Anu Roshini would like to acknowledge the financial support received from BITS, Pilani – K K Birla Goa Campus, India.