ISSN No. : 2394-0344 **REMARKING :** VOL-1 * ISSUE-1*JUNE-2014

Template Synthesis of Nano-/Microstructures and Devices

Ranjeet Singh
Assistant Professor
Deptt. of Physics
Rajiv Gandhi Govt. College,
Saha , Ambala

Abstract

Among various bottom-up techniques, the "Template Synthesis", using electrochemical/electroless deposition is one of the most important processes for manufacturing nano-/microstructures, nano-composites and devices and is relatively inexpensive and simple. The technique involves in using membranes- track etch membranes, anodic alumina membranes, besides other types of membranes as templates. The parameters viz., diameter as well as length i.e., the aspect ratio, shape and wall surface traits in these membranes are controllable. In the present paper, a detailed review of this technique, template synthesis of nano-/microstructures and devices will be presented.

Keywords : Template Synthesis, Nano-/microstructures, Track-Etch Membranes, Anodic Alumina Membrane.

Introduction

Nanotechnology is usually referred to as the technology of the study of objects in the size range of ~1-100 nm. Design, fabrication and applications of nanostructures and nanomaterials fall under the realm of nanotechnology and it is strong future requirement of the society. It is well known that revolution in digital world has been made possible by integrated circuits [1]. Even in the integrated circuits usage, there are continuous demands of high computing speeds, improved performance, low power consumption and lower cost which can be met by increasing packing densities of integrated circuits, reducing the size of devices [2, 3]. Packing densities continuously increased due to improved in design tools and IC fabrication techniques but the shrinkage of basic devices further will start to become problematic because of limitations associated with indefinite reduction in size and improvement of design tools. The nearer-term alternative for continuing to increase the packing density, speed of information processing and to keep the Moore's law alive is to use devices made of nano-sized materials.

The word nanotechnology has become popular during last few decades and is used to describe a variety of techniques to synthesize and characterize materials, functional structures and devices on a scale much smaller than one micron [4, 5]. In the recent time, nanotechnology has become a vital area of research and main focus of this research is the design, fabrication, characterization and application of nanomaterials and nanostructures. These structures include quantum dots, nano-particles, nanowires, nanofibres, nano-tubules, nanocrystals, nanofilms etc. Nano-sized materials show great variety of interesting properties such as catalytic, electrical, magnetic, optical etc. and this is the main driving force of the research in the field of nano-technology today [6]. Also due to these unique properties, the nanomaterials are used in numerous applications.

This article addresses Template Synthesis (TS) technique used for the synthesis of nano-/microstructures and devices. The recent past has witnessed keen interest being generated on the use of TS in the production of nano-/microstructure and devices.

Nanostructure Fabrication Approaches

There are two general approaches to fabricate nano-/microstructures . (a) top-down which includes to breakdown a bulk material to smaller pieces using mechanical, chemical or some other form of energy, (b) bottom up approach includes the synthesis of nanostructures atom by atom, or molecule by molecule via suitable routes like chemical reactions allowing for the precursor particles to grow in size. Attrition or milling is a typically top-down approach whereas colloidal dispersion, large polymer molecules, crystal growth etc. are better examples of bottom up approach in the fabrication of nanostructures. Lithography can be considered as a hybrid approach. Both approaches play an important role in the fabrication of nanostructure/nanomaterials in modern industry. The bottom up approach is a better choice than top-down approach as later may result into surface imperfections, which can affect significantly, the physical and chemical properties of synthesized nanostructues.

Template Synthesis is very general method to fabricate nanowires, nanotubels and nanorodes of metal, semiconductor, conducting polymers and carbon nanotubes. A template may be defined as central structure within which a network is formed in such a way that removal of template creates filled cavities with morphological features related to those of the template. Different kinds of templates including positive template, negative template, and surface edge have been used to fabricate nanostructures.

In negative template method, membrane type materials are used. Commonly used and commercially available positive templates are track etch membranes, anodic alumina membranes, porous silicon and carbon nanotubes [7-10]. The filling of pores of template with desired material can be done by galvanic and non-galvanic depositions which include electrochemical deposition, electroless deposition, direct chemical deposition, chemical vapour deposition, sol-gel deposition, pressure injection method etc [11-15]. Electrochemical deposition and direct chemical deposition are most widely used methods to create metal and semiconductor nano/micro structures [16, 17].

Positive template method uses wire like structures such as DNA, carbon nanotubes, polymer chains etc. On the outer surface, the material is deposited to the desired dimensions and, hence wire like or tube like nanostructures can be produced.

The **surface step-edge templates** include selective deposition of the material on the defect sites of the substrate. Zach et al., and Walter et al., synthesized nanowires at the step edges of HOPG [18, 19].

Negative Template Synthesis

A widely used technique to synthesize metallic, semiconducting, alloys, metal-semiconductor heterostructures, conducting polymers, CNT etc. is based on various templates. The principle of template based synthesis is producing components through use of replication i.e. die casting or mold casting just like making ice candies using molds.

Negative template based synthesis is the most suitable method to fabricate nano-/micro dimensional structures having high aspect ratio, desired morphology and geometry which are difficult to synthesize by conventional lithography [20]. In this method, we use pre-fabricated nano-/micro pores in the solid materials and nano-/micro wires with a predetermined diameter, of different materials can be synthesized by just filling the pores with desired material, either by galvanic or non- galvanic technique. Free standing nano-/micro wires can be obtained by dissolving host solid materials. A membrane with pre-fabricated pores or cavities of known morphology, number distribution and configuration may act as negative templates, the pores of which can facilitate replication by suitable means. The removal of host by some chemical means would lead to availability of structures whose morphology and stereo-chemical features and traits might replicate the cavities or pores of the membrane/template [16, 17, 21]. There are various negative templates viz TEMs, AAMs, glasses, mica sheets and diblock polymers that have been fabricated and used in template based synthesis of nano-/micro structure [8, 22-25].

Template Synthesis of Nano-/Micro Structures and Devices

The processes involved in the synthesis of nano-/micro structures and devices are important for the development of material science and engineering. There are many methods that have been developed for the synthesis of nano-/micro structures, ranging from milling techniques to chemical and lithographic methods. Because of high cost, slow throughput and low yield, the conventional fabrication techniques are not often synergistic with nano-synthesis. As a result, non-traditional techniques, drawing upon chemical methods, have emerged as serious competitors to non-lithographic and other traditional techniques. Template synthesis is elegant approach for the generation of nano-/micro structures such as nanowires and tubules via replication of desired material into the pores of template by galvanic and non-galvanic deposition strategies. It is a membrane based technology which makes use of templates as host materials for the deposition of the desired materials such as metals, conducting polymers, semiconductors, carbon naotubes (CNTs) and other materials. Two types of porous membranes viz track etch membranes (TEMs) and anodic alumina membranes (AAMs) are generally used for template synthesis of nano-/microstructures which are true replication of pore geometries. The nano-/micro structures so fabricated are cylindrical, conical, double conical, and tapered depending upon pore size, shape and geometry, with complete control over aspect ratio using galvanic and non-galvanic methods [22, 26]. The nano-/micro structures and devices can be freed and collected by dissolving host membrane using suitable solutions. Historically, the method of template synthesis was pioneered by Possin who prepared different metallic wires with diameter as small as 40 nm into the pores of TEMs and further, this method has been used by many researchers for the synthesis of nano-/micro structures [27]. The two representative strategies used in our laboratory for template synthesis of nano-/micro structures are discussed below.

Electrochemical Deposition

Electrodeposition is one of the most widely used methods to fill conductive materials into the pores of template using alternating current source or direct current source. Sometimes alternating current source is preferred over direct current source because of impedance barrier layer at the nano-hole bottom may be too large to afford for dc electrodeposition. The process of electrodeposition is preceeded by coating one face by metal thin film as cathode for electroplating. The volume of pore is continuously filled up starting from pore bottom thus resulting in control over length of nano-/microwires. After dissolving host template, free standing array of nano-/micro structure can be collected. The whole process of electrodeposition is illustrated schematically in the figure 1. The nano-/micro structures of metal, semiconductor and conducting polymers can be synthesized using this method. Here, the electrochemically deposited structures may be solid, or hollow, wires or tubules, depending on the material, the chemistry of the pore wall and the proper electrodeposition conditions [28]. This method is more advantageous due to avoidance of vacuum systems, its high flexibility and low cost as well as applicability to all substances suitable for deposition through electroplating and also due to much control on aspect ratio. Possin fabricated wires of Zn, In and Sn of diameter 400A^0 and 15 µm length using this technique [27]. Zong et al., synthesized Ag nanowires of diameter 35 nm via ac electrodeposition into the pores of AAM [29]. Whitney et al., reported the fabrication of Co and Ni nanowires having diameter 30-60 nm into the pores of TEM [11]. The electrochemistry of template synthesis of nanowires was studied by comparing the potentiostatically measured current-time characteristics obtained during wire growth of different pore dimensions and a pore-size dependence of the diffusion coefficient for the metal ions was found [30].

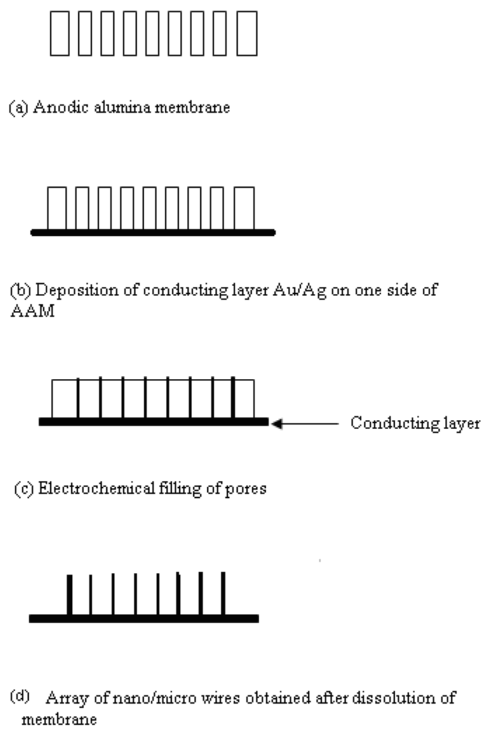

Figure 1 Schematic Diagram of Electrochemical Deposition [17].

Piraux et al., and Ansermet have reported the fabrication of magnetic nanowires, magnetic multilayered nanowires (Co/Cu, Ni/Cu) by using TEMs and AAMs as templates [31, 32]. Xu et al., also successfully prepared the nanowires of group II-VI semiconductors such as CdS, CdSe and CdTe in AAMs via ac electrodeposition method [33]. Schonenberger et al. (1997) have reported conducting polypyrrole synthesized electrochemically using TEMs [12].

Direct Chemical Deposition

Another technique for synthesis of semiconductor nanowires is by direct chemical reactions into the pores of template using two- compartment cell. The template/membrane is sandwiched between two compartments and one compartment is filled with cation precursor solution (A) while other is filled with anion precursor solution (B). Under suitable conditions of temperature and solutions concentration, the chemical reaction takes place between two solutions through the pores, resulting into the deposition of materials (A_mB_n) within the pores of templates. CdS and CdSe nanowires were synthesized by this technique [17, 34]. Polypyrrole nano/microstructures were synthesized by using direct chemical reaction into the pores of membrane [35].

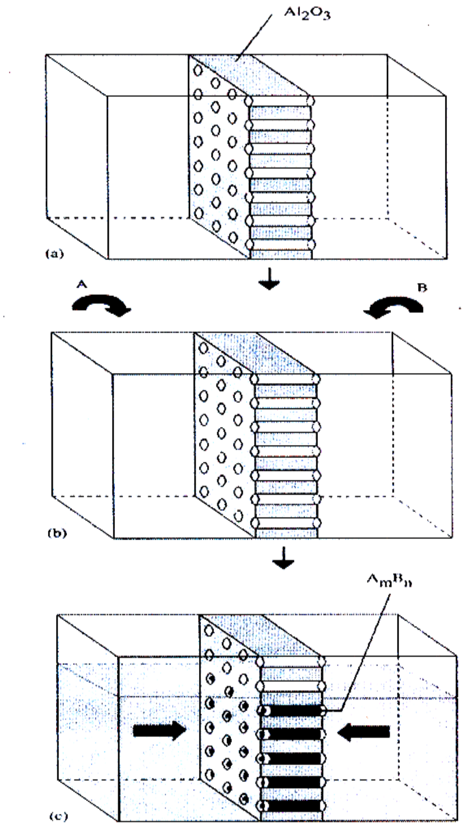

Figure 2. Schematic Diagram of Direct Chemical Deposition [16]

Conclusion

Template synthesis is very convenient approach for the synthesis of variety of nano-/micro structures and devices within the pores of template. The underlying principle of template synthesis approach is akin to that of producing components through the use of replication like making ice candies using molds.

References

1. Mead C., and L. Conway (1979), Introduction to VLSI systems, Addison-Wesley Longman Publishing Co., Inc. Boston,MA, USA.
2. Streetman B. and S. Banerjee (2005), Solid state electronics devices, (sixth ed.), Prentice Hall Series in solid state Physics, ISBN-9780131497269.
3. Rabaey J. M., A. Chandrakasn and B. Nikolic (2002), Digital integrated circuits: A design perspective, (second ed.), Prentice Hall Electronics and VLSI Series, ISBN-9780130909961.
4. Feynmann R. P. (1960), There's plenty of room at the bottom, Eng. Sci **23,** 22.

5. Smith R. (2004), Nanotechnology: A brief technology analysis, CTOnet.org.
6. Nalwa H. S. (2004), Encyclopedia of nanoscience and nanotechnology, Amrican Scientific Publishers, New York, USA.
7. Fleischer R. L., P. B. Price and R. M. Walker (1975), Nuclear tracks in Solids: Principles and Applications. Univ. of Calif. Press, Berkeley, CA.
8. Furneaux R. C., W. R. Rigby and A. P. Davidson (1989), The formation of controlled porosity membranes from anodically oxidized aluminum, Nature **337**, 147.
9. Guerret-Piecourt C., Y. Le Bouar, A. Loiseau, and H. Pascard (1994), Relation between metal electronic structure and morphology of metal compounds inside carbon nanotubes, Nature **372,** 761.
10. 10. Ajayan P. M., O. Stephen, P. Redlich and C. Colliex (1995), Carbon naotubes as removable templates for metal oxide nanocomposites and nanostructures, Nature **375**, 564.
11. Whitney T. M., J. S. Jiang, P.C. Searson and C. L. Chien (1993), Fabrication and magnetic properties of arrays of metallic nanowires, Science **261,** 1316.
12. Schonenberger C., B. M. I. Vander Zande, L. G. J. Fokkink, M. Henny, C. Schmid, M. Kruger, A. Bachtold, R. Huber, H. Birk and U. Staufer (1997), Template Synthesis of Nanowires in Porous Polycarbonate Membranes: Electrochemistry and Morphology, J. Phys. Chem. B **101**, 5497.
13. Shen X. P., M. Han, J. M. Hong, Z. Xue and Z. Xu (2005), Template-based CVD synthesis of ZnS nanotubes arrays, Chemical Vapor Deposition **11 (5),** 250.
14. Limmer S. J., S. Seraji, M. J. Forbess, Y. Wu, T. P. Chou, C. Nguyen and G. Z.Cao (2001), Electrophoretic growth of lead zirconate titanate nanorods, Adv. Mater. **13,** 1269.
15. Lee K. –B., S. –M. Lee and J. Cheon, (2001), Size-controlled synthesis of Pd nanowires using a mesoporous silica template via chemical vapor infilteration, Adv. Mater. **13,** 517.
16. Ranjeet Singh, Rajesh Kumar, S K Chakrvarti (2008), Non-galvanic template synthesis of CdSe nanowires using Anodic Alumina Membrane and their optical band gap determination, Mater. Lett. **62,** 874.
17. Ranjeet Singh, Rajesh Kumar, S.K. Chakarvarti (2008), Size effect on I–V characteristics of low dimensional metal– semiconductor heterojunctions, Physica E **40**, 591
18. 1Zach M P, K. H. Ng and R. M. Penner (2000), Molybdenum nanowires by electrodeposition, Science **290**, 2120.
19. Walter E. H., B. J. Murrey, F. Favier, G. Kaltenpoth, M. Grunze and R. M. Penner, (2002), Noble and coinage metal nanowires by electrochemical step edge decoration, J. Phys Chem B **44**, 11407
20. Hadjipanayis G. C. and R.W. Siegle (1994), Nanophase Materials: Synthesis, Properties, Applications, Series E: Applied Sciences, Kulwer, Dordrecht.
21. Chakarvarti S. K. and J. Vetter (1998), Template synthesis - A membrane based technology for generation of nano/micro materials: a review, Radiat. Meas. **29 (2)**, 149.
22. Spohr R.(1990),IonTracksand Microtechnology: Principles and Applications, Vieweg, Germany.
23. MacDowell A. A., E. L. Raab, W. T. Silfvast, L. H. Szeto, D. M. Tennant, W. K. Waskiewicz, P. P. Nguyen, D. H. Pearson, R. J. Tonucci and K. Babcock (1998), Fabrication and characterization of uniform metallic nanostructures using nanochannel glass, J. Electrochem. Soc. **145**, 247.
24. Nguyen P. P., D. H. Pearson, R. J. Tonucci and K. Babcock (1998), Fabrication and characterization of uniform metallic nanostructures using nanochannel glass, J. Electrochem. Soc. **145**, 247.
25. Thurn-Albrecht T., J. Schotter, G. A. Kaestle, N. Emley, T. Shibauchi, L. Krusin-elbaum, K. Guarini, C. T. Black, M. T. Tuominen and T. P. Russell (2000), Ultrahigh density nanowire arrays grown in self-assembled diblock copolymer templates, Science **290**, 2126.
26. Martin C. R. (1994), Nanomaterials: A membrane-based synthetic approach, Science **266,** 1961.
27. Possin G. E. (1970), Methods for forming very small diameter wires. Rev. Sci. Instum. **41**, 772.
28. Bao J., Z. Xu, J. Hong, X. Ma and Z. Lu (2004), Fabrication of cobalt nanostructures with different shapes in alumina template, Scripta Materiala **50,** 19.
29. Zong R .L., J. Zhou, Q. Li, B. Du, B Li, M. Fu, X.Qi, L. Li and S. Buddhudu (2004), Synthesis and optical properties of silver nanowires array embedded in anodic aluminamembranes,m J. Phys. Chem.B **108**, 16713.
30. Tang B. Z. and H. Xu (1999), Preparation, alignment, and optical properties of soluble poly(phenylacetylene)-wrapped carbon nanotubes, Macromolecules **32,** 2569.
31. 31. Piraux L., J. M. George, J. F. Despres, C. Leroy, E. Ferain and R. Legras (1994), Giant magetoresistance in mabnetic multilayered nanowires, Appl. Phys. Lett. **65**(19) 2484.
32. Ansermet J. P. (1998), Perpendicular transport of spin-polarized electrons through magnetic nanostructures, J. Phys.: Condensed Matter **10**, 6027.
33. Xu D., D. Chen, Y. Xu, X. Shi, G. Guo, and y. Tang (2000), Preparation of II-IV group semiconductors nanowire arrays by dc electrochemical deposition in porous aluminum oxide templates, Pure Appl. Chem., **72**, 127.
34. Ranjeet Singh, Vijay Kumar, S. K. Sharma and S. K. Chakarvarti (2008), Characterization of Non-Galvanic Synthesized CdS and CdSe Nanowires Via Anodic Alumina Membrane as Template, Journal of Scientific Conference Proceedings **1**, 53.
35. Sanjeev Kumar, D.L.Zagorski, Shyam Kumar, S.K.Chakarvarti (2004), Chemical synthesis of polypyrrole nano/microstructures, J. Mat. Sci. Lett. **39**, 6137.