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PREPARATION AND STUDY OF MAGNETIC PROPERTIES OF ULTRA HIGH DENSITY ARRAY OF MAGNETIC MATERIAL (Fe-Ni) QDOTS USING ANODIC ALUMINUM OXIDE (AAO) FILM

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Abstract
A summary of findings the growth of highly ordered magnetic material (Fe-Ni) quantum dots in porous Anodic Aluminum Oxide film is presented. In this experiment two step anodization processes is carried out to get highly ordered pore arrays. The Fe-Ni quantum dot arrays are fabricated by Chemical Vapor Deposition (CVD). The Anodic Aluminum Oxide template pore arrays and quantum dot arrays were observed using Scanning Electron Microscope (SEM), Vibrating Sample Magnetometer (VSM).

Key Words-Anodic Aluminum Oxide, quantum dots, quantum confinement, two step anodization, Scanning electron microscope, Vibrating sample magnetometer.

I. INTRODUCTION
Highly ordered nanohole arrays can be produced on a scale of several tens of nanometers through self-organization and have a diversity of applications, such as high density storage media, functional nanomaterials exhibiting quantum size effect, highly sensitive chemical sensors, nano electronic devices and functional bio-chemical membranes. One of the challenging directions in the field of nanotechnology is the fabrication of quantum dots [1] in which material properties changes dramatically due to arising of quantum effects [2] from the confinement of the electron [3] and holes in the material. Other material properties such as electrical and non linear optical properties [4] of material are also very different from those of materials bulk form.

Magnetic nanoparticles can have the special characteristic of exhibiting single-domain magnetism and can be used in magnetic tapes, ferrofluid, magnetic refrigerants, etc, because of their ultra fine size dimensioned with magnetic domain size [5]. Oxide coated iron nanoparticles are non-toxic materials and due to enhanced magnetic properties can be more effective as compare with magnetite nanoparticles for biomedical application [6],[7].

Anodic Aluminum Oxide (AAO)[8] is a well known nano technique in the field of research such as quantum dots, carbon nanotubes (CNT), metallic nanowires etc. Masuda and Fakuda first reported an ordered pore arrangement in porous anodic alumina in 1995 that can be used as a template for nanowire deposition [9]. This oxide has ordered hexagonal cells, where each cell contains nearly a cylindrical pore at its middle, as shown in Fig. 2. The structure of self ordered AAO has been known to form during the transformations of aluminum into alumina by volume expansion and mechanical driving forces. Anodic oxide coating for aluminum and aluminum alloys containing various acidic electrolytes has been explored since the early 1900s, and widely used as tableware, kettle, car body and other commodities. When aluminum is anodized in an acidic electrolyte under controlled conditions, (temperature, voltage, time etc.) aluminum forms a porous oxide called anodic aluminum oxide with very uniform and parallel cell pores [10]. The structure of AAO looks like a closely packed array of columnar cells. AAO is more sensitive to boundary conditions. So defects may appear under unsuitable conditions like electrolyte temperature and composition, applied voltage, chemical etching etc. So care must be taken during the fabrication of AAO. Anodized aluminum oxide film when grown in the appropriate acid electrolyte possess regular and highly anisotropic[11] porous structure with pore diameter ranging from 5 to about 100 nm, and with a density of pores ranging from 10^9 to $10^{11}/cm^2$. These characteristics allow a certain capability for the design of the pore features making the porous AAO templates an interesting substrate for nanotechnological applications. Porous alumina can be fabricated electrochemically through anodic oxidation of aluminum by means of

such a self-organization method, yielding highly ordered arrays of nanoholes several hundreds down to several tens of nanometers in size. The AAO templates with smaller pore diameters can be fabricated by anodizing the aluminum in low anodic potentials (about 10V or less). This produces a rather thin barrier layer, which can easily broken by thermal shock during electro deposition [12] because of its low mechanical strength. As a result it seems that there is an optimum barrier thickness for a given electro deposition voltage. The barrier layer thickness can be adjusted by additional electrochemical process at the end of anodizing process. By this modification, barrier layer can be thinned or thicken to the desired thickness required for electro deposition process. During the anodizing temperature must be controlled precisely. Anodizing temperature higher than 5^0C can cause barrier layer break down. A crack in barrier layer can cause non uniform deposition of quantum dots during the process of deposition. Since the pore diameter can be controlled in the range of ten to several hundred nanometers there fore porous anodic alumina is an ideal template for fabrication of ordered arrays of nanostructured materials.

II. PROCEDURE

The experimental procedure contains two steps.

A. *Fabrication of AAO films*

Following steps were followed to fabricate AAO template

(1) A high super pure(99.9%) Aluminum substrate (allowed impurities: Cu 0.003wt.%, Si 0.002 wt.%, Fe 0.004wt.%) having thickness of 1 micrometer was cut into sheets of required size.

(2) These sheets are cleaned in acetone and annealed in an air furnace at 550^0C with a heating rate of 3^0 C/minute.

(3) The sheets are then electro polished in a mixture of perchloric acid and ethanol (HCl_4 **:** C_2H_5OH = 1 **:** 4 by volume) for 5 minutes with a 30 V DC at a temperature less than 298K.

(4) The first anodization process was carried out in 0.3M oxalic acid solution at 2^0C for 225 minutes at an applied voltage of 40V. By this process a porous alumina film is developed.

(5) The above porous alumina film was removed by soaking it in a mixture of 35 ml/l , 85% phosphoric acid (H_3PO_4) and 20 gm/l acid anhydride of chromic acid other wise known as chromium trioxide (CrO_3) at 80^0C for 50 minutes.

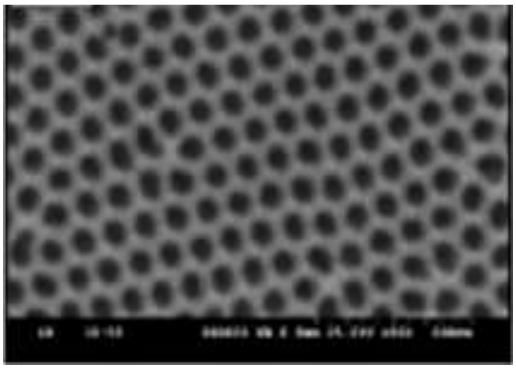
(6) The anodization process was repeated using the solution from the first anodization under the same conditions of the first step anodization.

(7) Aluminum substrate was removed by soaking in a solution of cupric chloride and hydrochloric acid (3 : 1 by volume) for 30 minutes.

(8) The transparent AAO membrane was immersed in a 0.1M phosphoric acid(H_3PO_4) solution at 60^0C for one and half hours to get a pore diameter of 40nm. How ever the pore diameter can be widened by increasing strength of phosphoric acid and the time of immersion..

The regularities of nanohole arrays formed by the second anodic oxidation were excellent. The pore size of the AAO membrane was examined by using Scanning Electron Microscope (SEM, Hitachi, S-3500N). The figure-1 shows SEM images of the surface of the AAO film after second anodization process. This AAO film has average pore diameter 40 nm and the pore density nearly 2.6 x 10^{11} pore/cm^2. The figure-2 shows cross sectional views of pores which indicate the formed nanopores can be comparatively homogeneous with out distoring the structure. The nanoholes are slightly enlarged by wet chemical etching with diluted phosphoric acid. The pore density in the film decreases when the work voltage increases. The nanopores exhibit almost perfect two dimensional arrays with a hexagonal pattern. Especially, hexagonal patterns are more apparent when the pore size is larger than 60 nm. In this image, we could confirm that around 40 nm nanopores can be prepared by immersing the sample in a 0.1 M phosphoric acid solution at 60^0C for one and half hours. The regularity of the nanohole array is the highest around 40V. The anodic voltage that gives a well-ordered nanohole array is found to be dependent on the acid species.

Fig.-1



SEM image of the AAO membrane fabricated by a second anodization process using a pore widening process for one and half hours. (Pore size about 40 nm.)

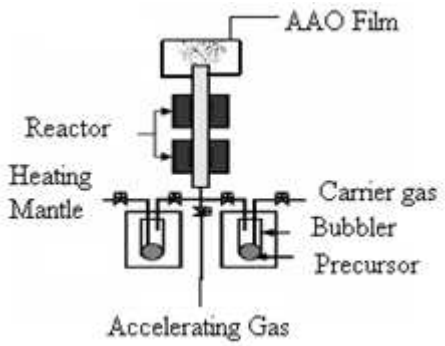
Fig.-2

B. *Deposition of Fe-Ni quantum dots*

Chemical vapor deposition (CVD) of materials in porous alumina nanoholes is a challenging topic for CVD researchers. Since porous alumina can contain extremely high aspect ratio holes, it is of great interest to discover how high aspect ratio of holes can be filled by CVD. This processes used to deposit quantum dots on a thin film. This method

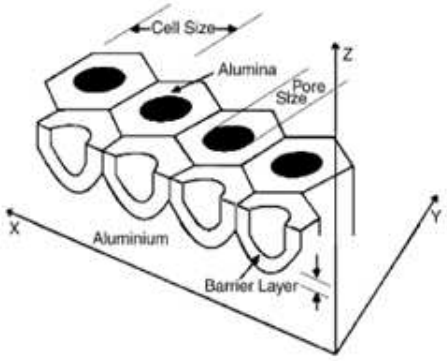
has tremendous flexibility in producing a wide range of materials and can take advantage of the huge database of precursor chemistries that have been developed for CVD processes. The precursors can be solid, liquid or gas at ambient conditions, but are delivered to the reactor as a vapor (from a bubbler or sublimation source, as necessary). Chemical vapor deposition (CVD) is a versatile process in which gas-phase molecules are decomposed to reactive species, leading to film or particle growth.CVD processes can be used to deposit a wide range of conducting, semiconducting, and insulating materials[13],[14]. A recent thrust [15],[16] of CVD techniques has been the controlled fabrication of qdots in porous hosts[17],[18].
The figure-3 shows a general process of CVD method to deposit nano particles on a slide.

Fig.-3



General scheme for CVD Process

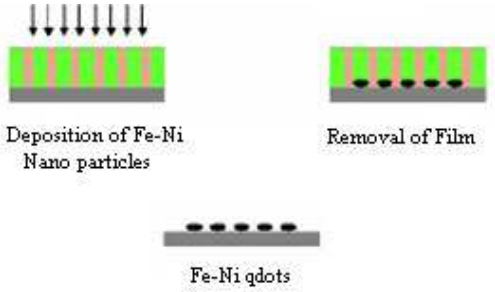
Here AAO film is taken to collect Fe-Ni quantum dots. In this case a carrier gas which is a mixture of high purity argon (instead of argon Helium may be used) and H_2 at 2000and 3000 sccm is fed through a heated bubbling unit containing the liquid precursor at the vaporization temperature. Here Ferrocene and nickelocene powders (Fe:Ni =



Schematic diagram of porous anodic alumina film on aluminum showing pores in cross section each in a

21.5**:**78.5, in mole ratio) were dissolved in $C_6H_3Cl_3$ to form a solution with a concentration of 0.06 g/ml and was taken as the liquid precursor. The flow of carrier gas entraining precursor vapor passed through the heated tubular reactor to the work chamber. The precursor decomposed in that reactor and condensed as particles on the anodized aluminum oxide film. After the deposition of Fe-Ni quantum dots the film was removed by etching and an array of qdots are collected. The figure-4 shows the schematic of Fe-Ni qdots fabrication on AAO film.

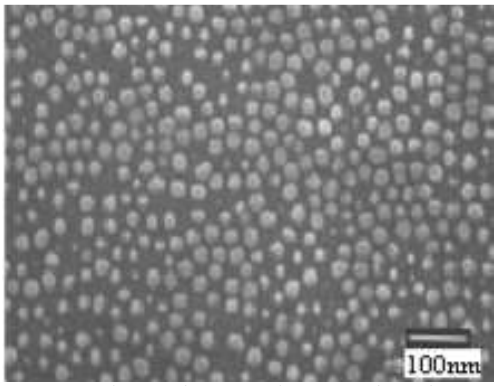
Fig.-4



Schematic of qdots array fabricated on AAO

Figure-5 shows SEM image of quantum dot arrays. The morphology of the prepared Fe-Ni qdots were observed and evaluated by Scanning Electron Microscope (SEM, Hitachi, S-3500N). The SEM technique was used to determine the grain size of the sample. The magnetization measurements were performed on a vibrating sample magnetometer (Lake Shore VSM-7307) at room temperature.

Fig.-5

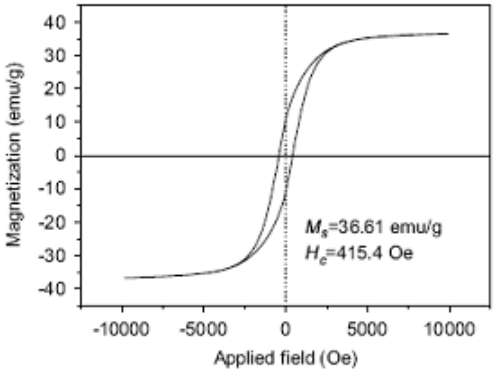


SEM image of quantum dot arrays of Fe-Ni

The VSM technique with an applied field -10000 Oe $\leq$ H $\leq$ 10000 Oe used to determine the magnetic properties of Fe-Ni qdots. The Fe-Ni nano structure has also been studied by X.W.Wei[19].

Fig.-6 shows the M-H hysteresis loop of the Fe-Ni qdots sample produced by using $C_6H_3Cl_3$ as a precursor.

Fig.-6



Hysteris curve of Fe-Ni qdots, where Ms and Hc are saturation magnetization and coercivity respectively

It can be seen from Fig.-6 that the Fe-Ni qdots show typical ferromagnetic properties. The saturation magnetization (Ms) obtained at room temperature is 36.61 emu/g and the maximum coercivity (Hc) obtained at room temperature is 415.4 Oe. The Curie temperature (Tc) of the Fe-Ni qdots sample is 650^0C, which is much higher than that of the bulk FeNi alloy (400^0C). This demonstrates that Fe-Ni qdots can be used as high-temperature magnetic materials.

III. CONCLUSION

Porous AAO templates with tailored pore density, diameter and length are confirmed as an interesting option to grow Fe-Ni qdots. SEM is a well suited technique for the characterization of the surface features of AAO film, the study of their internal pore structure The anodization voltage plays a fundamental role in the shape of the pores and, consequently, in the shape of the Fe-Ni qdots. Hexagonal pores are obtained when the AAO template is developed by the two-step method and below a threshold voltage value which in this experiment is about 40 V when oxalic acid is used as anodizing agent. In conclusion, Fe-Ni qdots were prepared by using $C_6H_3Cl_3$ as precursor. Magnetic measurements on the sample show typical ferromagnetic properties, with saturation magnetization Ms = 36.61 emu/g and coercivity Hc = 415.4 Oe. Theoretical calculation[20] show that, when the coating thickness is 2.5 mm, the largest reflection loss and band width of below 5 dB of the as-grown Fe-Ni qdots sample are 16.9 dB and 5.2 GHz, respectively. This demonstrates that Fe-Ni qdots are promising to be used as an effective absorber for electromagnetic waves with thinner coating thickness. Magnetic measurement[21] of Fe-Ni qdots reveals that it is super magnetic before calcinations and ferromagnetic after calcinations which demonstrate that the properties of Fe-Ni qdots were very different in respect to Fe-Ni bulk alloy. These Fe-Ni qdots which are magnetic qdots could be used for the memory device applications and can be used in magnetic tapes, ferrofluid, magnetic refrigerants etc. This method can be used to fabricate other nano particles and carbon nano tubes of different size depending on the pore size.

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REFERENCES:-

[1] P.Michler, Single Quantum Dots: Fundamentals applications and new concepts. Topics in applied physics, Vol.90 (Springer, Berlin,2000).
[2] Stephanie M. Reimann, Matti Manninen, Electronic structure of quantum dots, Reviews of Modern Physics Volume 74, October 2002.
[3] M.Grundmann, Nano Optoelectronics: Concepts, Physics and devices(Springer, Berlin,2002)
[4] U.Woggon, Optical properties of Semiconductor quantum dots(Springer, Berlin, 1997.
[5] G.C. Hadjipanayis, G.A. Prinz, Science and Technology of Nanostructured Magnetic Materials, Plenum, New York, 1991.
[6] Y. Zhang, N. Kohler, M. Zhang Surface modification of superparamagnetic magnetite nanoparticles and their intracellular uptake. Biomaterials;23:1553–1561(2002).
[7] O. Bomatr -Miguel, Marra P. Morales, Pedro Tartaja, Jesurs Ruiz-Cabellob, Pierre Bonvillec, Martɔrn Santosd, Xinqing Zhaoe, Veintemillas-Verdaguera S. Fe-based nanoparticulate metallic alloys as contrast agents for magnetic resonance imaging. Biomaterials; 26: P. 5695–5703(2005).
[8] L. Malkinski, A. Chalastaras, A. Vovk, J. Jung, E. Kim, J. Jun, and C. Ventrice, Jr., "Magnetoresistive Multilayers Deposited on the AAO Membranes," J. Magnetism and Magnetic Mater., 286 108-112 (2005).
[9] H. Masuda, K. Fukuda, Science 268 , 1466(1995).
[10] J. P. O' Sullivant and G. C. Wood, Proc. Roy. Soc. Lond. A. 317, 511-543 (1970).
[11] A. Balandin, K.L. Wang, N. Kouklin and S. Bandyopadhaya, Appl. Phys. Lett. 76, 137(2000).
[12] A.Saedi, M. Ghorbani, Material chemistry and Physics 91,417-427(2005).
[13] Rai, Akhilesh ; Chaudhary, Minakshi ; Ahmad, Absar.; Bhargava, Suresh & Sastry, Murali. Synthesis of triangular Au core-Ag shell nanoparticles. Mater. Res. Bull., 2007, 42(7), 1212-220.
[14] M. L., Jensen, K. F., Eds.;Chemical Vapor Deposition; Hitchman, Academic Press: San Diego, CA, 1993.
[15] Bowes, C. L.; Makek, A.; Ozin, G. A. Chem. Vap. Deposition 1996, 2, 97.
[16] Li, W. Z.; Xie, S. S.; Qian, L. X.; Chang, B. H.; Zou, B. S.; Zhou, W. Y.; Zhao, R. A.; Wang, G. Science 1996, 274, 1701.
[17] Kyotani, T.; Tsai, L.-F.; Tomita, A. Chem. Mater. 1996, 8, 2109.
[18] Kyotani, T.; Tsai, L.-F.; Tomita, A. Chem. Mater. 1995, 7, 1427.
[19] Wei Xian-Wen, Zhu Guo-Xing, Zhou Ju-Hong and Sun Hui-Qun 2006 *Materials Chemistry and Physics* 100 481–5.
[20] Ohring.M. The Material science of Thin Films; Academic Press: New York, 1992.
[21] A.M.Davarpanah, A.A. Mirzae, M.Sargazi and M.Feizi, Journal of Physics: Conference series 126(2008)012065