Magnetic thin film formation on the surface of solution induced via island growth of nanoparticles

Pawan Kumar[1], Subhash Chander Katyal[2], Sunil Kumar Khah[1], Nitin Rawat[3] and Rajesh Kumar[1,*]

[1]*Jaypee University of Information Technology, Waknaghat, Solan (H.P) 173234, India*
[2]*Jaypee Institute of Information Technology, Sector 128, Noida (U.P) 201304, India*
[3]*Gwangju Institute of Science and Technology (GIST),Oryong-dong, Buk-gu, Gwangju 500712, South Korea*

[*]Corresponding author. Tel: (+91) 1792-239386; E-mail: rajesh.kumar@juit.ac.in, rajeshkumarf11@gmail.com

ABSTRACT

Thin magnetic films have been formed on the surface of Fe^{2+}, Fe^{3+} and PVA solution applying NH_3 vapors. The growth of films has been inferred via island growth mechanism. The film grown for shorter exposure time of NH_3 is composed of islands in nanometer range, whereas the film grown for high exposure time of NH_3 consists islands in micrometer range. For lower NH_3 exposure, discrete islands are formed in polyvinyl alcohol (PVA) matrix which coalesces in bigger islands when exposed for larger time to NH_3 vapor. Similarly, depending upon the NH_3 exposure, nanoparticles inside films vary from 5 to 30 nm. The magnetization measurement shows that the films have thickness dependent saturation magnetization. For the thick film the saturation magnetic field is around 1400 Oe whereas for thin film it is 1000 Oe. Copyright © 2013 VBRI press.

Keywords: Island growth; magnetic thin film; NH_3 exposure; glass substrate.

Pawan Kumar graduated from Govt. Degree College Mandi (H.P) in 2007 and Master of Science from H. P. University, Shimla (India) in 2009. Currently he is working as a Ph.D. student in the Department of Physics, Jaypee University of Information Technology, Solan (India). His current research work is on the synthesis and characterization of magnetic nanoparticles thin films.

S. C. Katyal joined Himachal Pradesh University, Shimla in 1982 and became Professor in 1998. He has also worked as the Chairman of the Department of Physics Himachal Pradesh University, Shimla in 2002. In 1986 he was awarded for Japan Society for the Promotion of Science (JSPS) Fellowship. In 2003 he joined Jaypee University of Information Technology, Solan (India) and worked as head of the Department till 2010. Since January 2011, he is working as a Professor in the department of Physics at Jaypee Institute of Information Technology, Noida (India). He has 44 research publications in the International/National Journals and 28 in international/National conferences. He has successfully supervised 4 Ph.D. and 9 Master of Philosophy (M.Phil.) students till date.

Sunil Kumar Khah received his B.Sc. (Electronic Sciences) from Kashmir University and M.Sc., M.Phil, and Ph.D. from Agra University. He did his postdoctoral research in the field of high power microwave component design from Institute of Plasma Research (IPR), India. Presently, he is working as a Professor in the field of Electromagnetics at Department of Physics, Jaypee University of Information Technology Solan (India). His research interest is numerical modeling of high frequency antenna designs and nanostructured antenna.

Rajesh Kumar did his Master of Science from C.C.S. University, Meerut (India) and Master of Technology from the Department of Physics in 2003 from IIT Roorkee (India). His PhD is awarded in the field of Nanotechnology from H. P. University, Shimla (India) in 2010. He is working as an Assistant Professor in the Department of Physics, Jaypee University of Information Technology, Solan (India). He has been researcher in the field of Nanotechnology at Center for Super-functional Materials at Pohang University of Science and Technology (POSTECH), South Korea. Currently he has his collaboration with Gwangju Institute of Science and Technology (GIST), South Korea. His areas of interest are synthesis, characterization and applications of transition metal nanostructures and application of nanostructure in optical microscopy.

Introduction

Among various magnetic materials the oxides of iron such as hematite, magnetite, and maghemite represent an important class of magnetic transition metal oxide materials. The most stable iron oxide under ambient conditions, hematite (α-Fe_2O_3) is used as catalysts, pigments, and gas sensors owing to its low cost and high resistance to corrosion. It can be used as the starting material for the synthesis of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), which have been used intensively for both fundamental scientific interest and technological applications. They are used in many technological applications such as high density magnetic storage, spintronic devices, biomedical applications, electromagnetic interference and sensors etc [1-2].

At room temperature, the normal stoichiometric forms of iron oxides are magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) in addition to their hydroxides. In maghemite and hematite, the iron cations are in the Fe^{3+} state but magnetite contains both Fe^{2+} and Fe^{3+} ions. Although enormous progress has been made in fabricating magnetic iron oxide thin films with controllable morphologies [3-6], it is still a key goal in modern materials science. In this work we have applied NH_3 vapors for different time intervals on the surface of the iron solution containing PVA. The island structures inside the film have been observed. These films have been characterized for structural and magnetic properties.

Experimental

A 0.4 g poly vinyl alcohol (PVA) was dissolved in 100 ml of distilled water with the help of magnetic stirrer. Ferrous chloride (0.3 g) and ferric chloride (0.6 g) were added to this solution followed by heating at 80 ^{o}C with magnetic stirring for 10 minutes. In order to form thin film, the iron chloride solution was taken in a petri dish. NH_4OH (50 %) was taken in a closed vessel to produce NH_3 vapors which using a nozzle were poured on the surface of Fe^{3+}/Fe^{2+} solution. The NH_3 vapors were exposed for different time. After exposure to the NH_3 vapor the solution surface turned into a thin film. The reaction was performed in argon gas environment. In this work, two exposure times 4 and 1 seconds for NH_3 vapors were randomly selected. The uniformly distributed iron oxide nanoparticles film was then separated from the solution on the glass substrate and dried under argon gas atmosphere at 50 ^{o}C in a horizontal tube furnace. Thus synthesized films have been investigated for morphological, magnetic and structural properties using scanning electron microscopy (SEM), atomic force microscopy (AFM), magnetic force microscopy (MFM), vibrating sample measurement (VSM) and X-ray diffraction (XRD) spectroscopy.

Results and discussion

Growth of thin film as well as the phase transformation involves the process of nucleation and growth on the growth surface. Here the films are grown on the surface of solution; therefore a heterogeneous nucleation mechanism is involved in the formation of films. In general, for heterogeneous nucleation to take place, two interactions play an important role in determining the initial nucleation and thus the film structure; (i) interactions among growth species and (ii) interaction of growth species with the surface. The island growth mechanism, one of the heterogeneous processes occurs when the growth species are more strongly bonded to each other than to the growth surface [7-9]. In our case as the films were grown on the surface of solution and are not uniform throughout as shown in **Fig. 1**, the most expected mechanism is island growth which involves strong interaction among the growth species rather than the surface and growth species. **Fig. 1** shows SEM images of the film after transferring onto the surface of the glass substrate. **Fig. 1** (a) and (b) are low and high magnification SEM images of film for high exposure time (4 seconds) of NH_3 vapor. Here islands are observed with size 50 to 300 nm. Similarly, **Fig. 1(c)** and **(d)** are SEM images for low exposure time (1 seconds), indicating the islands with size 10 to 100 nm. Further, at higher magnification the size of the particles inside the islands are observed from 5 to 30 nm.
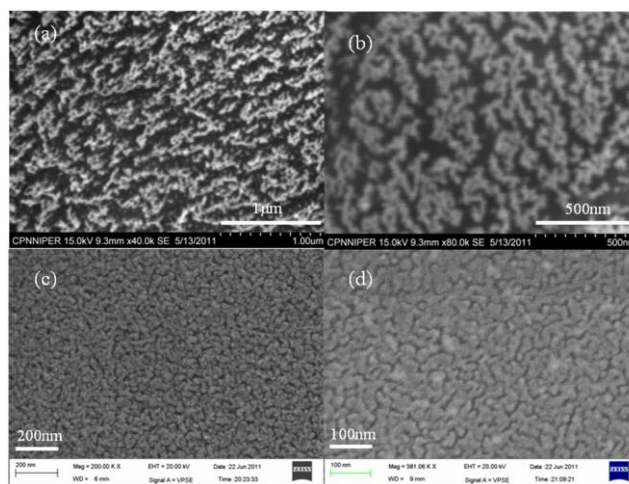
Fig. 1. SEM images of the films after transferring onto the surface of glass substrate; **(a)** & **(b)** for high exposure time of NH_3 and **(c)** & **(d)** for low exposure time of NH_3.

In case of large time exposure of NH_3 vapors, big size islands form due to the formation of larger size magnetic nanoparticles. For lower flow of NH_3 vapors the film consists of small islands uniformly dispersed in PVA matrix. Another approach for the explanation of the island growth of the film may be based upon their magnetic nature. Since the particles inside the films are magnetic in nature therefore, the interaction among the particles would result in island structure formation. These larger nanoparticles in thick film due to strong attractive interaction may easily form large size islands after aggregation. For low time exposure of NH_3 vapors, small size nanoparticles are formed on the solution surface which forms islands due to the interaction between them. The small size of islands for low time NH_3 exposure may be attributed due to the presence of PVA matrix which prevents the growth of islands. Further the mechanism of the film formation on the surface of the solution can be explained by the cross linking of the PVA chain with Fe^{2+} ions. The addition of Fe^{2+} ions in the solution will form

coordinate bond or hydrogen bond with –OH group of one or more chains of PVA on the surface of the solution resulting in the cross linking of PVA chain on the solution surface [10]. The surface morphology of the films was further studied by the AFM. **Fig. 2** shows a two dimensional AFM images of thick and thin films on the glass substrate.
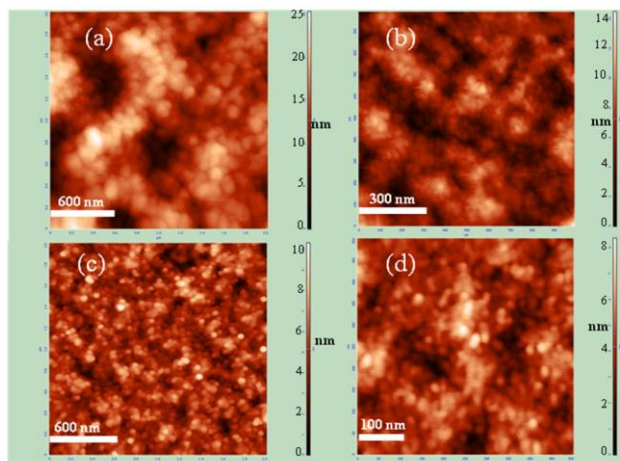
Fig. 2. AFM images of the films on the glass substrate; (a) & (b) for high exposure time of NH_3 and (c) & (d) for low exposure time of NH_3.

The root mean square value of roughness is 4 nm for higher NH_3 exposure (**Fig. 2(a)** and **2(b)**) and 1.2 nm for low NH_3 exposure (**Fig.2(c)** and **2(d)**) the corresponding average grain sizes are 12 nm, 5 nm, respectively. The island in the form of the cluster of particles is also observed**.** For lower NH_3 exposure, the film is comparatively smoother than that for high exposure time. **Fig. 3** is MFM image indicating islands in the films. The grain like structures can be observed for both high and low exposure times of NH_3 (**Fig. 3** (a) and (b)), indicating films to be magnetic in nature.
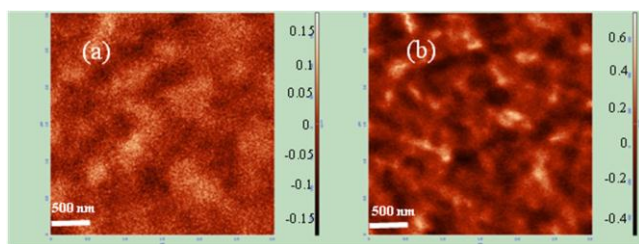
**Fig. 3.** MFM images indicating islands in the films; (a) for high exposure time of NH_3 and (b) for low exposure time of NH_3.

We used VSM technique for magnetic properties measurement. **Fig. 4** shows the MH measurement at room temperature (300 K) for thick and thin films with magnetic film sweeping back and forth between -6 kOe and 6 kOe. The saturation magnetization is around 1.1×10^{-3} emu for thick film and 0.4×10^{-3} emu for thin film. From the MH measurement the saturation magnetic field for the thick film is 1400 Oe while thin film gets saturated at 1000 Oe. This is probably due to the presence of large size iron oxide nanoparticles for the longer time NH_3 exposure as compare to shorter time NH_3 exposure. Further, it may be attributed

that a stronger magnetic field is required to align all the magnetic moments of the larger particle as compared to the smaller one in the films.

From **Fig. 4,** it is clear that the thin film saturation magnetization is increased by very small amount for the increasing magnetic field. This may be attributed to the presence of larger size particle or the anisotropy within thin film. Because the small particles are aligned at lower magnetic field but larger particle can saturate at higher magnetic field. So the magnetization seems to be increased with the magnetic field.
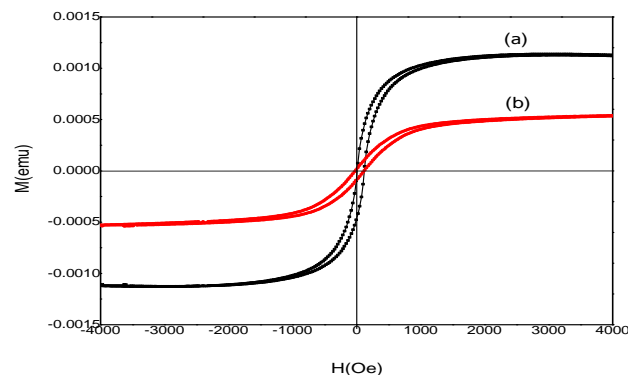
Fig. 4. MH measurements of films on glass substrate; **(a)** for high exposure time of NH_3 and **(b)** for low exposure time of NH_3.

For structural properties the films were investigated using X-ray diffraction (XRD) using CuK_α(1.54 Å) source and scanning the angles from 10 to 60 with step size 0.0330. From the XRD data for a film for high exposure of the NH_3 (**Fig. 5**), a strong peak at $2\theta = 33.33^{\circ}$ corresponding to hematite (α-Fe_2O_3) and a small peak at $2\theta = 35.48^{\circ}$ coresponding to magnetite (Fe_3O_4) are observed. The formation of α-Fe_2O_3 is due to the formation of iron hydroxide on the surface of solution which on heating form hematite (α-Fe_2O_3).
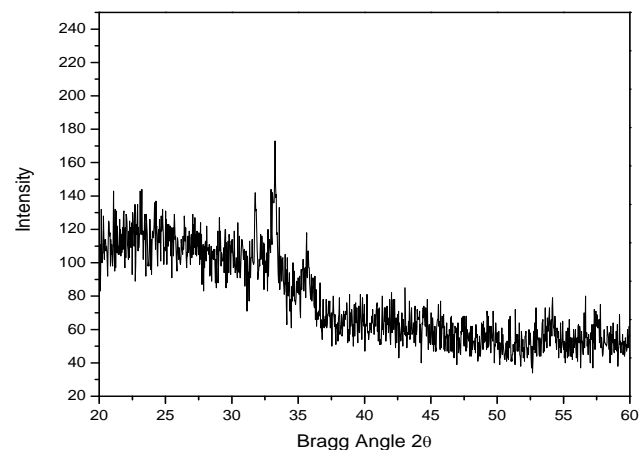
Fig. 5. XRD pattern of the film on the glass substrate for high exposure time of NH_3.

Conclusion

Magnetic thin films have been formed on the surface of solution by using a very simple and straight method. Island

growth results due to the magnetic interaction among the initially formed magnetic nanoparticles. The thickness of the magnetic film may be easily controlled by controlling the exposure of the NH_3 vapors. This is an easy one step method and may be applied for the formation of other films utilizing NH_3 vapors. Once the film is formed on the surface of the solution it may be transferred to any substrate of interest.

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