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Modification of spin coating method and its application to grow thin films of cobalt ferrite

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Spin coating method has been modified to widen its scope for applications. The film deposition assembly is suitably designed. With this modification, it is possible to use common inorganic chemicals in the form of their aqueous solutions as starting materials to grow thin films of binary/ternary oxides. This method is applied to grow thin films of cobalt ferrite. The structure, morphology and magnetic properties of thin films of cobalt ferrite have been determined by using X-ray diffraction, Scanning electron microscopy and vibrating sample magnetometer respectively. The results show that the present technique is useful to deposit thin films of cobalt ferrite, which are qualitatively comparable to the films grown by other wet chemical techniques. © *2003 Kluwer Academic Publishers*

1. Introduction

Several methods to grow thin films of inorganic compound semiconductors are taking vital roles in the advancement of technologies. To obtain precision in the performance of thin film based devices, control over the film properties is necessary. Therefore, many sophisticated techniques namely, vacuum evaporation [1], sputtering [2], molecular beam epitaxy [3], laser assisted vacuum evaporation [4] etc. are being used. These processes are energy intensive and involve high temperature. These sophisticated methods have merit in having control over film growth and consequently the properties of thin films. However, researchers also studied wet chemical processes from the economic considerations and some other advantages namely, simplicity and low temperature processing etc. Spin coating [5] is widely applied amongst many wet chemical processes namely chemical bath deposition [6], electrodeposition [7], Langmuir Blodgett technique [8], spray pyrolysis [9], liquid liquid interface reaction technique [10], sol-gel process etc. [11].

The vital parameters for the applications of spin coating method are (i) viscosity of the precursor solution and (ii) spin speed. The viscosity of aqueous precursor solution is not suitable for the application of spin coating. This brings serious limitations to spin coating method. It forces the use of costly organometalic precursors in organic solvents jeopardizing the advantages of spin coating method. To overcome this limitation, we address to a major modification to the spin coating technique to deposit thin films. The modified process can also be applied to form thin films of organic materials by processing their aqueous/organic solutions. Such thin films of organic materials have potential applications in various devices [12]. The modified process has been tested successfully for producing binary/ternary oxide thin films namely ZrO_2, SnO_2, $BaPbO_3$, $CoFe_2O_4$ and an organic compound namely anthracene. However, in the present communication we report the studies on cobalt ferrite thin films formed by modified spin coating method.

Initially, we describe the modification of spin coating process and apply this technique to grow thin films of cobalt ferrite. The choice of cobalt ferrite was based on its importance as a potential candidate for magnetic, magneto-optical recording media and its magnetostriction properties. The low coercivity of cobalt ferrite films is detrimental for the applications of recording media. However, it was concieved that by controlling the microstructure and particle size, the coercivity can be enhanced [5]. The wet chemical methods are known to control the microstructure and the particle size. Therefore, it was decided to apply modified spin coating technique to deposit thin films of cobalt ferrite suitable for the applications as recording media. Achieving high coercivity in a cubic cobalt ferrite is crucial for technological applications as well as understanding of basic physics (macroscopic quantum tunneling of magnetization as an example).

The methods of preparation of cobalt ferrite thin films reported in the literature are sputtering [13], sol gel [11], vacuum evaporation technique [14], chemical vapour deposition [15], solid state reaction of vacuum evaporated layers [16] etc. Most of the techniques require sophisticated equipment. A simple technique such as spin coating has been applied for the purpose of film formation in the sol gel process [17]. The present communication reports the exclusive use of spin coating

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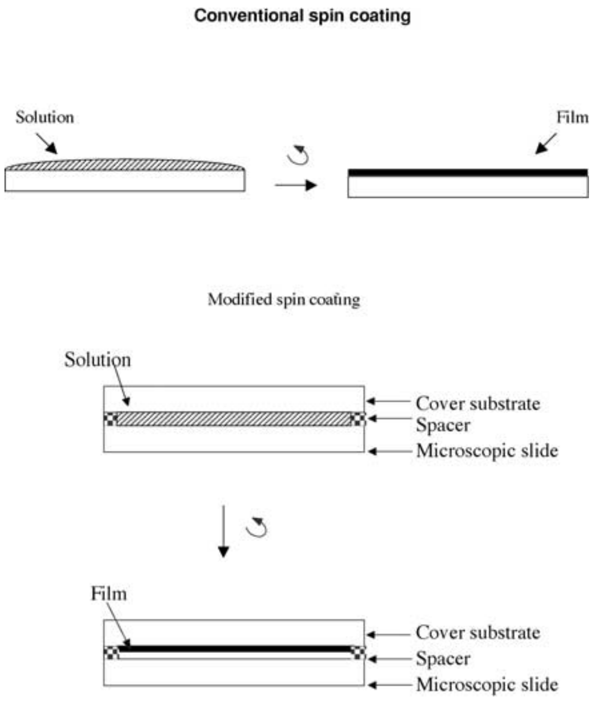

Figure 1 Schematic illustration of the spin coating method.

technique wherein aqueous salt solutions are used for the formation of thin film of important ternary oxides namely cobalt ferrite. The magnetic properties of these films are also presented.

1.1. Description of modified spin-coating method

In the conventional spin coating process [5], the viscosity of precursor sol/solution in the range of 4–10 cp (centi poise) is a prerequisite and spinning speed is a dependent parameter. This brings serious limitations to its application, as the viscosity of aqueous sol/solution is not suitable. Therefore use of costly solutions of organometalic precursors in organic solvents become inevitable. Alternatively, an aqueous precursor solution with certain additives for viscosity adjustment [18] become necessary and complicates the process.

Fig. 1 gives the conventional and modified assembly for spin coating. The modified assembly is made up of a tandem of two substrates separated by spacers between them and maintaining a uniform gap of 1–3 mm. This assembly can be fixed on a rotatable support chuck having an axis of rotation passing through the center of gravity of the said assembly. The space between the parallel plates consisting of microscopic slide substrate and a cover substrate is used as a reservoir to place aqueous precursor solution leading to the formation of desired precursor solid film on the substrate when subjected to spin processing. All other procedural features are the same in conventional spin coating and its modification.

In principle the modified process has a general applicability for producing binary-ternary oxide thin films and also for other types of films where aqueous precursor is available.

2. Experimental

All chemicals of reagent grade from S. D. Chemicals Ltd were used without further purification. Double distilled deionized water was used in all experiments.

Fig. 1 shows the modified spin coating assembly. It consists of a base substrate having spacers to keep cover substrate at a fixed desired distance from the base substrate. This whole assembly is fixed on a rotatable support chuck with an arrangement to spin the assembly at desired rate.

An aqueous solution containing cobalt nitrate and iron nitrate is prepared so that $Co^{++}:Fe^{+++}$ ratio is $1:2$. The base substrate is flooded by the solution so that cover substrate (quartz) is in contact with it. This assembly is subjected to spinning operation (3000 rpm, 60 seconds). A mixture of fine crystallites of cobalt nitrate and iron nitrate coats cover substrate uniformly. The cover substrate is then heated to various temperatures from 500 to 750°C for fixed time (2 hrs). The structural characterization of cobalt ferrite films was done by X-ray diffraction (XRD) using Philips XRD system with Cu K_α radiation. Surface morphology of the films was studied using a Leica Cambridge (Stereoscan 440) scanning electron microscope (SEM). The micrographs of the samples were recorded with a 20 kV EHT (Electrical High Tension) and a 25 pA (pico Ampere) camera attached on the high-resolution recording unit. Magnetic properties determination of films was done by using vibrating sample magnetometer model EG and G, PAR 4500. Thickness of the film was determined using Taly Step measuring instrument Taylar Hobson (UK).

3. Results and discussion

In the conventional spin-coating process, if aqueous solutions of precursors are used, no coating on the substrate could be obtained. During the spinning process, solution along with solute is physically thrown away from the substrate surface by the centrifugal force. Thus film formation by crystallization of precursors does not take place. This can be attributed to low contact time of spinning solution with the substrate surface.

Centrifugal force overcomes the forces, which are responsible to maintain the contact between a solution and the substrate surface. These forces mainly consist of surface tension and viscosity that are characteristic properties of the materials.

In the modified spin coating method, the centrifugal force that arises when this assembly is spinning would be of the same order as in the conventional spin coating assembly. But the fluid dynamics of the modified assembly is indeed complex. Researchers have studied the fluid dynamics for the flow of fluid between rotating parallel plates. Abbot and Walters [19] have obtained an exact solution for the Newtonian fluids, and Rajagopal [20] has considered a second order fluid. It is to be noted that the modified assembly is not exactly a parallel plate viscometer, but the study by Abbott and Walters has some relevance for the modified assembly. Without going into the fundamentals, it would be safe to assume that the fluid held between the two substrates gets stabilized due to secondary flow which along with the surface tension overcomes the influence of the centrifugal force. Therefore the loss of the fluid is due to the evaporation alone. This slow evaporation of the fluid initiates the crystallization/gelation/precipitation of the molecules in a thin film form. It is observed that cover

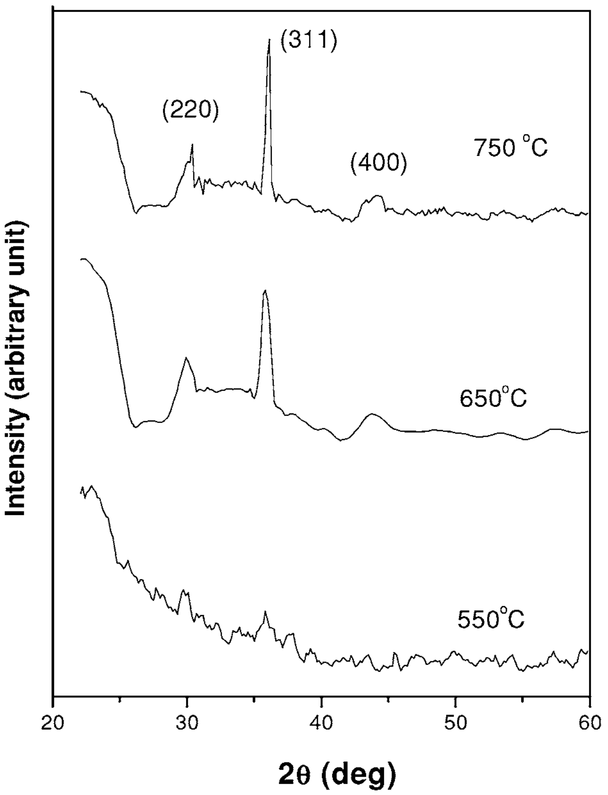

Figure 2 X-ray diffraction pattern for $CoFe_2O_4$.

substrate is uniformly coated as compared to the base substrate. The process of recrystalization is considerably fast and therefore the deposited material consists of fine crystallites. The solute in the present studies is a mixture of cobalt nitrate and ferric nitrate having $Co^{+2} : Fe^{+3}$ in the ratio 1 : 2. When the aqueous solution of cobalt nitrate and ferric nitrate mixture is subjected to the modified spin coating process, the cover substrate is coated with the fine crystallites of a mixture of cobalt nitrate and ferric nitrate. The crystallization is so fast that preferential crystallization is practically absent and co-crystallization of the mixture of cobalt nitrate and ferric nitrate occurs. The crystallite size of the mixture of nitrates is very small. No peaks in XRD could be observed for the deposited mixture of nitrates. The coating of mixed co-crystallized nitrates on calcination decompose at high temperature to their respective oxides. The mixture of freshly formed oxides would be highly reactive. On calcination at high temperature, the mixture of iron oxide and cobalt oxide reacts to form cobalt ferrite.

Fig. 2 shows the evolution of XRD of the film when heated at various temperatures. Although at temperature of 550°C, there is a broad peak corresponding to the (311) peak of $CoFe_2O_4$, the distinguishable intensity for three peaks as shown in Fig. 2 is achieved only when film is annealed at 750°C. This temperature is lower than the required temperature for the formation of Co-ferrite in the conventional ceramic and sol-gel spin coating methods. The formation of Co-ferrite at low temperature is in accordance with that reported by Cheng *et al.* [21] where, such lowering in the annealing temperature is ascribed to the short distance diffusion of metal ions, required for the formation of the spinel phase.

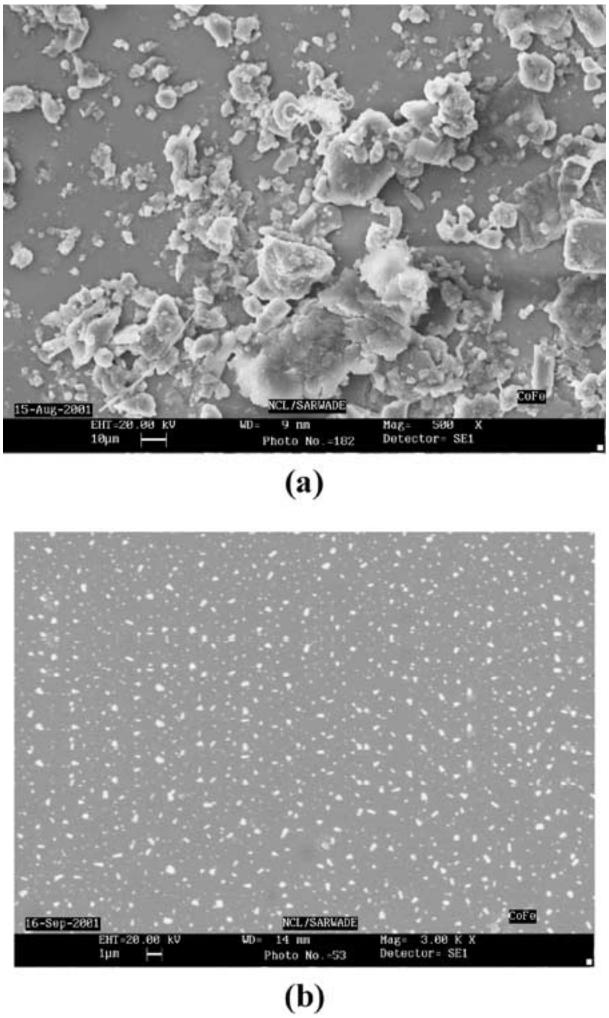

Figure 3 (a) SEM of the precursors; (b) SEM of the $CoFe_2O_4$ particulate film.

The formation of Co-ferrite at low temperature as indicated by XRD studies was supplemented from the DSC studies of mixed nitrates. The DSC curve (Figure not shown) showed that the nitrates decompose at around 350°C as indicated by the characteristic endotherm followed by the reaction of decomposition products, namely cobalt oxide and iron oxide, beginning at the temperature of 430°C, as indicated by the characteristic exotherm. The exotherm is broad, as the reaction is diffusion controlled.

Fig. 3 shows the microstructure of the precursor mixture and that of the ferrite. It is evident that there is a distinct morphological change. The relatively larger particles with some agglomerate in the precursors (Fig. 3a) decompose to the respective oxides. These oxides on diffusion form $CoFe_2O_4$ in the film form, with the particle size in the sub-micron range. The lower temperature of formation has helped to limit the growth of particle and maintained the uniformity of film morphology, avoiding agglomeration, as evident from Fig. 3b. It is possible, therefore to control the particle size of $CoFe_2O_4$ film by monitoring the time and temperature of reaction. This is a special feature that $CoFe_2O_4$ thin films with uniform particle size in submicron range are obtained by the present method.

Fig. 4 is the hysteresis loop of the cobalt ferrite thin film deposited on quartz substrate. The comparison of

TABLE I Comparison of the properties of $CoFe_2O_4$ thin films formed by various methods

Method	Processing temperature (°C)	H_c (Oe)	M_s (emu/cc)	Reference
Magnetron sputtering system	Annealing temperature at 1000°C. (a) Si substrate; (b) Suphire substrate; (c) Quartz substrate	(a) 3000–4000 (b) 1200; (c) 3000–4000	300	[22]
Sol-gel spin coating	Annealing at 850°C, film on Si substrate	2550	–	[24]
Sol-gel spin coating	Annealing at 850°C, film on Si (100) substrate	2000	–	[5]
Sol-gel modified Pechini method	Annealing at 800°C, film on Si (100) substrate	1400 (Kerr hystereis)	–	[21]
Chelating sol-gel process	Rapid annealing at 900°C, on corning glass substrate with YSZ buffer layer	3000	400	[23]
Modified spin coating method	Annealing at 750°C films on quartz substrate	2820	320	Present communication

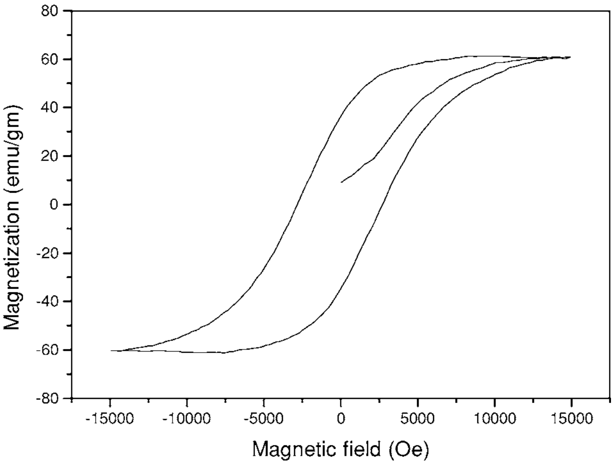

Figure 4 Magnetization as a function of magnetic field for $CoFe_2O_4$.

magnetic properties of Co-ferrite films formed by various other methods and the present method is shown in Table I.

The coercivity recorded was approximately 2820 Oe, which is considerably high [13] as required for memory applications. This may be due to the smaller particle size, as is evident from SEM studies. Lim *et al.* [15] have observed the degradation of magnetic properties when the film was deposited in absence of buffer layer (YSZ) between the substrate and the film. In the present studies, the high value of coercivity is observed without the use of buffer layer. High value of coercivity ($H_c = 3000$–4000 Oe.) has also been reported by Ding *et al.* [22] where $CoFe_2O_4$ films were deposited on Si or SiO_2 substrate, and the increase in Hc was attributed to the SiO_2 diffusions into Co-ferrite films. However, it may be noted that the diffusion of SiO_2 may be facilitated at high processing temperature of 1000°C as against relatively lower processing temperature of 750°C in the present study.

In plane and perpendicular measurement of our film, show small difference in the coercivity values. Perpendicularly applied field shows slightly higher values of H_c than that for in plane measurement. (not shown in Figure) The difference is small and therefore the film can be considered as isotropic. The quartz substrate is noncrystalline and therefore the unoriented film leading to isotropy is understandable [23].

The magnetization M_s of the film has a reasonable value of 300 emu/cc which is also encouraging however other known important parameters such as effect of substrate on the film/orientation, degree of inversion, effect of doping etc. demand further studies. It would need detailed data acquisition and analysis, hence would be dealt separately.

4. Conclusions

The modified spin-coating method wherein aqueous precursor solutions are used for spinning is a versatile technique for the preparation of binary and ternary oxides. This method has advantages over the conventional methods in respect of simplicity, wide range of applicability and low temperature formation of thin films of oxides with low particle size. These advantages are well proven in the present study of the thin films of Co-ferrite prepared by modified spin coating method with encouraging properties namely coercivity 2820 Oe and saturation magnetization 320 emu/cc.

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