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Preparation and magnetic properties of the $CoFe_2O_4$ thin films on Si substrate by sol-gel technique

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A stable precursor for $CoFe_2O_4$ thin film was prepared by sol-gel technique from the aqueous solution of $FeCl_3{\cdot}6H_2O$ and $CoCl_2{\cdot}6H_2O$. Sol was deposited on a naturally oxidized silicon-substrate by spinning technique (2000 rpm) and heat treated at different temperatures ranging from 700 to 1100 °C. Thickness of the films was controlled in the range of 400–500 nm and all the films were characterized by using XRD and SEM. The effects of temperature and the composition on the formation of $CoFe_2O_4$ thin film were also studied. Films obtained at relatively lower temperature showed multi-phases of α-Fe_2O_3, $CoFe_2O_4$ and CoO while the formation of $CoFe_2O_4$ phase increases with increasing temperature. Furthermore, the composition of the solution in mol% has great role on the formation of $CoFe_2O_4$ films and the film containing 50 mol% of Co^{2+} exhibited $CoFe_2O_4$ mono-phase. Surface morphology of the films was studied by scanning electron microscope (SEM). Magnetic properties of the films, studied by using vibrating sample magnetometer (VSM), showed relatively high saturation magnetization (8.04–22.21 kWb/m^2) as well as high coercivity (44.59–63.30 kA/m). Saturation magnetization also increases with increasing heat treatment temperature.

1. Introduction

Currently the preparation of ferrite materials has received much attention due to their considerable importance to the electronic materials industries [1–5]. Several types of ferrite materials have been investigated for this purpose. Cobalt ferrite ($CoFe_2O_4$) is a cubic oxide which has large magneto-crystalline anisotropy ($K_1 = +2 \times 10^6$ erg/cm^3) and also high saturation of magnetization (33.44 kWb/m^2) [6–8]. The optimal structure for the enhanced magnetic properties of Co ferrite is the perfect inverse spinel [9], in which the octahedral B sites are occupied by 8 Co^{2+} and 8 Fe^{3+} cations, while the tetrahedral A sites are occupied by the remaining 8 Fe^{3+} cations. Furthermore, it has high chemical stability and mechanical hardness, and thus is a good candidate for high-density recording media [7–9]. Though the properties of bulk materials have been well studied and utilized in magnetics technology, the study of the growth and properties in thin film form has not carried out to the same extent [9–22]. Several methods, such as pulsed laser deposition [15–18], vacuum deposition [19], sputtering [20] and sol-gel processing [12–14, 21, 22] have been employed for the preparation of such thin film.

Out of these methods, the sol-gel technique using an aqueous solution, has emerged recently as a versatile method for synthesizing thin films of different inorganic materials because it is possible to develop thin films with good homogeneity in a cost effective way [13]. The main advantage of this method is not only the reduction in the annealing temperature required for crystallization process but also the good control of the formation of ferrite particles with small grain size that will be required for high-density recording media [8]. The choice of starting material as well as the substrate for developing ferrite thin films is also an important factor. It is important to mention here that the Si is widely used as the substrate for electronic devices and it is very difficult to prepare uniform ferrite thin films on Si substrate from aqueous precursors by this method. This is because the viscosity of the aqueous solution is not suitable for the application of spin coating technique especially on Si substrate. This is mainly due to the presence of oxide layer on the surface of the Si

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substrate. Again, most of the work reported in this area so far used nitrate salts as the starting materials. Therefore, the main objective of this work is to develop $CoFe_2O_4$ thin film on Si substrate using chloride salts as starting materials. It is expected that the use of chloride salts would facilitate the formation of ferrite materials. In this context, the present work describes the preparation of $CoFe_2O_4$ thin films on naturally oxidized Si (110) single crystalline substrate by sol-gel technique using the aqueous solution of the corresponding metal-chloride salts. The study of the magnetic properties of the coated films is also described in this paper.

2. Experimental

Required amounts of $FeCl_3 \cdot 6H_2O$ (99% GR) and $CoCl_2 \cdot 6H_2O$ (99% GR) were dissolved in water by stirring at ambient temperature and the polyvinyl alcohol (PVA, 1.5 wt%) was added to the solution. The mixture was again stirred at about 70°C for 1 h to dissolve the polyvinyl alcohol and aqueous NH_3 solution was added drop-wise to adjust pH. The pH of the solution was fixed to about 1.5 to 2.5 because the stability of the sols was seriously dependent on pH. It was observed that the sols become unstable above pH = 4, which may be due to the formation of corresponding hydroxide at higher pH. To change the Fe^{3+}/Co^{2+} ratio, several sols were prepared with different compositions (Co^{2+} = 33–50 mol%). The sols were aged for 48 h at ambient temperature and were deposited on naturally oxidized Si (110) single crystalline substrates by spinning at 2000 rpm. The substrates were ultrasonically cleaned with distilled and ion exchanged water prior to the spinning. The deposited films were dried at 90°C for 30 min in air followed by 190°C for another 30 min in air. All the films were heated at 500°C to decompose the organic additives (polyvinyl alcohol) and heat treated at different temperatures between 700 to 1100°C for 1 h in air.

There are several parameters which affect the stability of the solution as well as the stability for application by spin coating method: (i) pH of the solution, (ii) concentration of the metal ions, (iii) preparation temperature, (iv) viscosity of precursor solution and (v) the rpm of the spin technique. The first three parameters affect the stability of the solution while the last two are important for the application by spin coating method.

It was found that the viscosity of the aqueous solution was not suitable for the application of spin coating technique especially on Si substrate. This might be due to the presence of oxide layers on the surface of the Si substrate. To overcome this problem, it was necessary to add some easily decomposable foreign materials. The polyvinyl alcohol (Mol. Wt., 22000) was found to be one such material because of its low decomposition temperature (300°C). It is also soluble in hot water and exhibited enough viscosity to have a good coating by spinning technique. Addition of polyvinyl alcohol to the precursor with a concentration of 1.5 wt% gave an appropriate viscosity in the range of 15 to 18 mPas.

Viscosity of the solution was measured at room temperature using a viscometer (model TV-20, Toki Sangyo Co. Ltd.). Thickness of the deposited films was measured using a surface profile meter (Kosaka Laboratory Ltd., model ET 350) and was in the range 400–500 nm after the deposition of two successive layers. Structural characterization of the films was done by X-ray diffraction (XRD) using Rigaku X-ray diffractometer (RINT 2500) with CuKα radiation ($\lambda = 1.54056$ Å). Surface morphology of the films was studied using a Hitachi S4300 field emission scanning electron microscope (FESEM) with 15.0 kV EHT (electrical high tension). The compositions of the films were determined by chemical analysis using inductive couple plasma (ICP) spectroscopy (Optima 2000 DV). For ICP analysis films were dissolved in concentrated HCl solution. Magnetic properties of the films were studied at room temperature using a vibrating sample magnetometer (TOEI Industries, model VSM-5).

3. Results and discussions

The XRD patterns for all the films showed many characteristic reflections. The reflections were characterized and identified as corresponding to the phases CoO, α-Fe_2O_3 and $CoFe_2O_4$. Fig. 1 shows the typical XRD

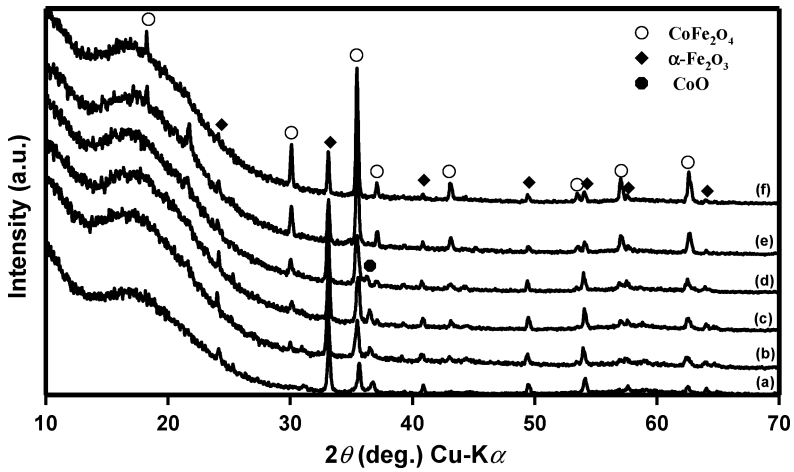

Figure 1 XRD patterns of the films with a stoichiometric composition (Co^{2+} = 33.3 mol%) deposited on Si substrate by spinning (2000 rpm) and heat treated at different temperatures for 1 h in air: (a) 500°C, (b) 700°C, (c) 800°C, (d) 900°C, (e) 1000°C and (f) 1100°C.

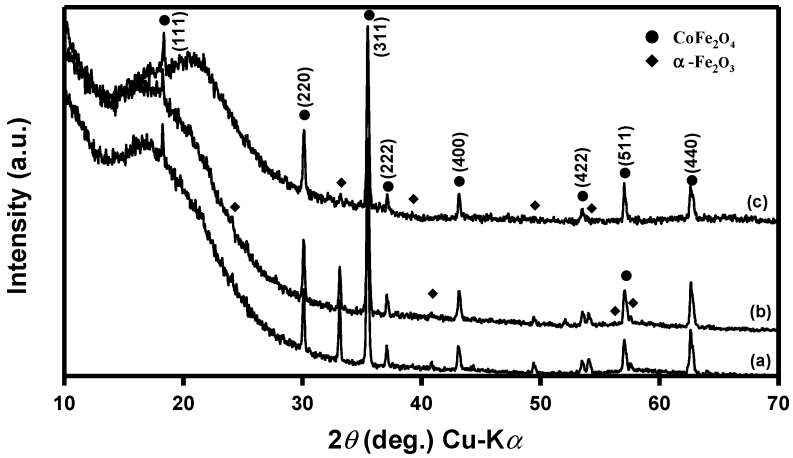

Figure 2 XRD patterns of the films with different Co^{2+} contents, deposited on Si substrate by spinning (2000 rpm) and heat treated at 1100°C in air for 1 h: (a) 33.3 mol%, (b) 42.8 mol% and (c) 50.0 mol%.

patterns of stoichiometric films (Co^{2+} = 33.3 mol%) obtained after heating at different temperatures. It was observed that XRD patterns of the films heated at temperatures between 500 to 900°C mostly corresponded to the α-Fe_2O_3 along with cubic $CoFe_2O_4$ phase. A trace of cubic CoO phases was also observed up to 900°C. No preferential orientation was observed even at the higher heat treatment temperatures. When the films were heated above 900°C (900–1100°C), the formation of $CoFe_2O_4$ phases predominated over α-Fe_2O_3 phases which was the clear indication of the transformation of α-Fe_2O_3 to $CoFe_2O_4$ at relatively high temperatures.

The point to be noted here is that the films obtained from the solution containing stoichiometric amount ($CoFe_2O_4$) of cobalt still contained the α-Fe_2O_3 phase, although it was heated at relatively high temperature (say, 1100°C). This clearly indicates that the solution composition has the great role on the formation of $CoFe_2O_4$. To investigate the effect of composition, three different sols with Co^{2+} content in the range of 33 to 50 mol% were prepared and deposited on the Si-substrates in a similar manner. Fig. 2 shows the XRD patterns of the film heat treated at 1100°C with different Co^{2+} content. It was observed that the film containing 50 mol% of Co^{2+} displayed almost single phase of $CoFe_2O_4$ with a slight trace of α-Fe_2O_3 phase.

The compositions of the films were analyzed by chemical analysis using ICP. It was found that the film compositions were close to those of the solution compositions. Based on the chemical analysis and the XRD results, the composition of the films may be predicted as $Co_{1+x}Fe_{2-x}O_4$ where $x = 0.3$–0.5. Crystallite sizes (D) of the films were also determined from XRD by using Debye-Scherer equation [23], $D = K\lambda/h_{1/2}\cos\theta$, where the constant K is 0.9, λ is the wavelength of the X-ray radiation (1.54056 Å) and $h_{1/2}$ is the diffraction broadening of the peak at half-height for a Bragg's angle θ. It was found that the particles were in the range 30–45 nm.

The surface morphology of all the films was studied by using high resolution FESEM. A representative micrograph of the film containing 42.8 mol% of Co^{2+} obtained after heating at 1100°C is shown in Fig. 3. The micrograph showed that the films were almost uniform throughout the surface of the substrates. Grain sizes of the film were also found to be in the range 60 to 140 nm which was higher than those of sizes that determined from XRD. This difference might be due to the agglomeration of the small grains being seen in the micrograph.

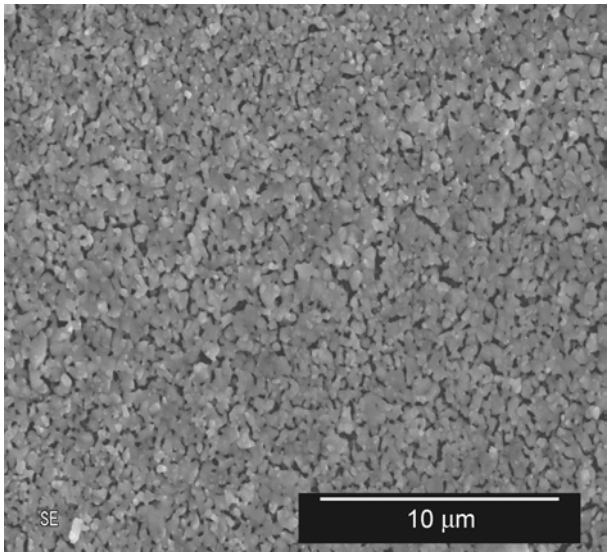

Figure 3 FESEM image of the film deposited on Si substrate by spinning (2000 rpm) and heat treated at 1100°C for 1 h in air. Co^{2+} content = 42.8 mol%.

Typical magnetic hysteresis curves both in-plane and perpendicular are shown in Fig. 4. The films exhibited moderate saturation magnetization and coercivity in the range 8.04–22.21 kWb/m^2 and 44.59–63.30 kA/m, respectively. The saturation magnetization values are lower than those of the $CoFe_2O_4$ bulk material (33.44 kWb/m^2) prepared by conventional solid state reaction [6–8]. However, the films seemed to have neither in-plane nor perpendicular magnetic anisotropy. It was observed that the films obtained at lower temperature (say 700°C) exhibited relatively higher coercivity (63.30 kA/m). The existence of high coercivity value at lower temperatures may be due to the presence of antiferromagnetic α-Fe_2O_3 and CoO particles,

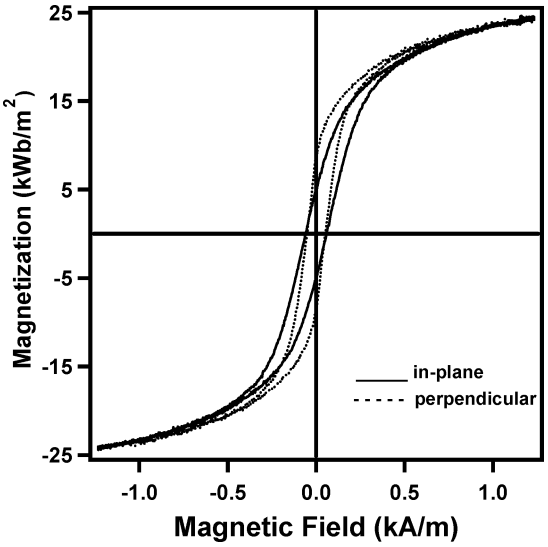

Figure 4 Magnetic hysteresis curves for the film (Co^{2+} content = 42.8 mol%) deposited on Si substrate by spinning (2000 rpm) and heat treated at 1100°C for 1 h in air.

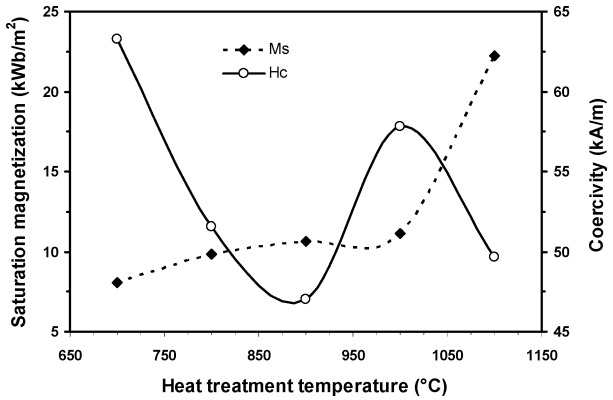

Figure 5 Effect of heat treatment temperature on the magnetic properties of the $CoFe_2O_4$ thin film deposited on Si substrate.

which are known to show very high coercivity. Fig. 5 shows the effect of heat treatment temperature on coercivity as well as saturation of magnetization. It was observed that the value of saturation of magnetization gradually increases with increasing heat treatment temperature.

4. Conclusion

Cubic phase cobalt ferrite ($CoFe_2O_4$) thin films (400–500 nm thickness) have been successfully prepared directly on Si-substrate by sol-gel technique. The effect of temperature on the formation of $CoFe_2O_4$ showed that the formation of $CoFe_2O_4$ started at lower temperature but completed at ∼1000°C. It was observed that the solution composition also plays a great role on the formation of $CoFe_2O_4$ whose formation is enhanced with relatively high Co^{2+}-content (50 mol%). The magnetic property measurement on the films revealed the presence of large saturation of magnetization (8.04–22.21 kWb/m^2) and its values increased with heat treatment temperature.

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