

Development of $\text{Co}_{1+x}\text{Fe}_{2-x}\text{O}_4$ ($x=0-0.5$) thin films on SiO_2 glass by the sol-gel method and the study of the effect of composition on their magnetic properties

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Abstract

Spinel-type $\text{Co}_{1+x}\text{Fe}_{2-x}\text{O}_4$ ($x=0-0.5$) thin films (~450 nm thickness) on SiO_2 glass substrate were prepared by the sol-gel method using spinning technique (2000 rpm) from the aqueous solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. All the films were heat treated at different temperatures ranging from 700 to 1100 °C. The films were structurally characterized by using the X-ray diffraction technique (XRD), and the morphology was studied by field emission scanning electron microscope (FESEM). The effects of temperature and the composition ($[\text{Co}^{2+}]/[\text{Fe}^{3+}]$ ratio) on the formation of $\text{Co}_{1+x}\text{Fe}_{2-x}\text{O}_4$ thin films were also studied. The films obtained at relatively low temperature showed mixed phases of $\alpha\text{-Fe}_2\text{O}_3$, CoO, along with CoFe_2O_4 , while the formation of the CoFe_2O_4 phase increases with increasing temperature. Furthermore, the composition of the solution in terms of $[\text{Co}^{2+}]/[\text{Fe}^{3+}]$ plays a great role on the formation and magnetic properties of the films. The magnetic properties of the films, studied using vibrating sample magnetometer (VSM), showed relatively small saturation magnetization, and coercivity was observed to be low as compared with that of other reports. Saturation magnetization also increases with increasing heat treatment temperature.

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1. Introduction

The development of thin films of functional ceramic materials has received much current interest due to their wide application and considerable importance in the electronic materials industries [1–5]. Spinel-type ferrite (MeFe_2O_4 , Me=Co, Ni, Zn, etc.) has been found to be one of the suitable candidates for this purpose due to their high saturation magnetization, high resistivity, excellent chemical stability and mechanical hardness [6,7]. In addition, CoFe_2O_4 is known to have large cubic magneto-crystalline anisotropy ($K_1=+2 \times 10^6$ erg/cm³) with three easy axes, [100] [8], and also exhibited large coercivity [6]. The structure of the CoFe_2O_4 is the perfect inverse spinel type [10], where the octahedral B sites are occupied by eight

Co^{2+} and eight Fe^{3+} cations, while the tetrahedral A sites are occupied by the remaining eight Fe^{3+} cations. This perfect inverse spinel structure enhances the magnetic properties of Co ferrite. The point to be noted here that the properties of $\text{Co}_{1+x}\text{Fe}_{2-x}\text{O}_4$ bulk materials have been studied intensively in last few decades [6–9,11–14] and they have been utilized in magnetic technology, especially to develop high-density recording media [7,15–17]. However, the development of thin film was not explored so much [10,18–21]. There are many reports that described the preparation and magnetic properties of such thin films by various methods, like pulsed laser deposition [22–24], vacuum evaporation [19,25], sputtering [26,27], chemical vapour deposition [28] and sol-gel processing [12,18,20,21,29–32], etc. Out of these methods, the sol-gel technique using 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 by a cost-

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effective way [18]. The main advantage of this method is not only to reduce the annealing temperature required for crystallization process but also to have good control over the formation of ferrite particles with small grain size, which will be required for high-density recording media [7]. It is worth noting that most of the electronic thin film devices required Si and SiO₂ as substrate, and it is difficult to prepare uniform ferrite thin films on these substrates, especially from aqueous precursors. This is because the viscosity of the aqueous solution is not suitable for the application of spin-coating technique on these type of substrates. Therefore, our objective is to develop Co_{1+x}Fe_{2-x}O₄ thin films on SiO₂ substrates using low-cost starting materials in a simpler way. Our earlier work has described the preparation and magnetic properties of CoFe₂O₄ thin film on naturally oxidized Si(110) substrate. Therefore, present work describes the preparation and magnetic properties of Co_{1+x}Fe_{2-x}O₄ thin films on SiO₂ glass substrate by sol–gel method from the aqueous solution of corresponding metal salts. This paper also describes the effect of composition ([Co²⁺]/[Fe³⁺] ratio) on the magnetic properties of the films.

2. Experimental

2.1. Preparation of precursor solution

FeCl₃·6H₂O (99% GR) and CoCl₂·6H₂O (99% GR) were dissolved in 20 ml of double-distilled water under stirring at ambient temperature. The composition of the solution (molar ratios of [Co²⁺]/[Fe³⁺]) were in the range 0.5–1.0. Polyvinyl alcohol (PVA, mol. weight: 22000, 1.5% w/w) was added to the above solution. The mixture was again stirred at about 70 °C for 1 h to dissolve the polyvinyl alcohol, and then aqueous NH₃ solution (4% v/v) was added drop-wise to adjust the pH in the range 1.5 to 2.5. The sols were allowed to age for 48 h at an ambient temperature.

2.2. Preparation of thin films

The aged sols were deposited on SiO₂ glass substrates by the spinning technique using 2000 rpm. The substrates were ultrasonically cleaned with distilled 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 (PVA). Two successive layers were deposited to obtain the film thickness about of 450 nm, and the films were heat treated at different temperatures between 700 and 1100 °C for 1 h in air.

2.3. Physical measurements

The viscosity of the solution was measured at room temperature using a TV-20 viscometer (Toki Sangyo). The

thickness of the deposited films was determined using ET-350 surface profile meter (Kosaka Laboratory). The structural characterization of the films was studied by Rigaku RINT 2500 X-ray diffractometer using CuKα radiation ($\lambda=1.54056$ Å). The morphology of the films was studied using a Hitachi S4300 field emission scanning electron microscope (FESEM) with 15.0 kV electrical high tension (EHT). The films were dissolved in concentrated HCl solution to determine the film compositions by chemical analysis using Optima 2000 DV inductive coupled plasma (ICP) spectroscopy. The conversion electron Mössbauer spectra (CEMS) of the sample films were measured using a handmade gas-flow counter in addition to the conventional Mössbauer instrument (Topologic Systems, MFD-110D). The velocity scale of the spectra was calibrated by an α-Fe foil. A VSM-5 vibrating sample magnetometer (TOEI Industry) was used to study the magnetic properties of the films, at room temperature.

3. Results and discussion

3.1. Preparation of precursor solutions and deposition of coating

Stable precursors for the development of CoFe₂O₄ thin films were prepared using corresponding metal salts solutions. The following parameters affect the stability of the sols, as well as the application of spin coating method: (i) pH of the solution, (ii) sol processing temperature, (iii) viscosity of sols and (iv) the rpm of the spinning technique. Out of these parameters, pH and sol processing temperature directly affect on the stability of the sols, while the viscosity and the rpm of spin-coating technique are important for the deposition of the sols on the substrates by spin-coating method. The thickness of the spin-coated films also depends on these two factors.

The pH is one of the most important factors for the preparation of stable sols from the aqueous precursors (metal salts solution). It helps to hydrolyze the metal salts to form colloidal hydroxides. The formation of hydroxides favors higher pH, but at the same time, it helps to grow the particles, which exceeds the colloidal limit causing precipitation. It was observed that the aqueous sols obtained from the aqueous solution of FeCl₃ and CoCl₂ become unstable above pH 4, which might be due to the formation of corresponding hydroxide with larger particle size at higher pH.

The viscosity of the aqueous solution is another important factor for the application of the spin-coating technique. The aqueous solution of the metal salts is not suitable for the spin-coating technique [21] because of their relatively low viscosity, which gives rise to poor surface wettability. The viscosity of the aqueous sols can be increased by adding some foreign additives, which should have the property to decompose easily at relatively lower temperature. The polyvinyl alcohol (PVA) is found to be the

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