

Structural and Morphological Properties of Free-Standing Cobalt Ferrite (CoFe₂O₄) Thin Films Via Liquid-Vapor Interfacial Method

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Abstract

Spinel ferrites-magnetic materials with unique crystal structures are widely used in various applications such as, spintronics devices, magnetic sensors, and high-density data storage. In this work, cobalt ferrite (CoFe₂O₄) thin films have been fabricated via liquid-vapor interfacial method, with an external magnetic field applied during the film formation. The films are formed without a substrate, which are freestanding and are grown in short span of time. The as formed CoFe₂O₄ thin films were transferred to glass substrates. Structural, morphological, and chemical bonding of the films have been analyzed by using X-ray diffraction (XRD), Field-emission scanning electron microscopy (FE-SEM), and Fourier-transform infrared spectroscopy (FTIR). The XRD reveals a crystalline growth, orientated in the direction of (220) plane. Lattice parameters appeared to be influenced by external magnetic field with crystallite size from 43.6 to 51.7 nm without and with the presence of external magnetic field, respectively. Surface topography of the films investigated by FE-SEM, indicates uniform thickness of the films. The FTIR analysis identified functional groups, metal-oxygen stretching vibrations (Fe-O, Co-O), bonding environment and cationic distribution.

Keywords: CoFe₂O₄, free-standing, NH₃ vapours, thin films.

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Introduction

Spinel ferrites (MFe₂O₄) due to their exceptional properties including optical, electrical, dielectric, magnetic, Curie temperature, permeability, and chemical stability have gained considerable attention. Their excellent resistance to oxidation and corrosion arises from their inherent stability and reliability in challenging environments, including chemical conditions [1]. The magnetic properties demonstrated by spinel ferrite have made them an essential candidate for modern devices such as spintronics [2] magnetic recording media [3], magnetic sensors [4], EMI shielding [5], and data storage [6]. The inherent high electrical resistivity and low eddy/dielectric loss make them useful in a variety of electrical devices, including telecommunication and microwave absorption [7-8]. The high Curie temperature allows them to maintain their intrinsic magnetic properties even at high temperatures [9] and is applicable for high-temperature applications such as,

high-frequency transformers and microwave devices. The magnetism determined in spinel ferrites depends on the metal cation occupancies in the octahedral and tetrahedral sites with the coordination of oxygen atoms. These lattice sites are unequally distributed in crystallographic structure, with divalent metal cations (such as Co²⁺, Ni²⁺, Zn²⁺, etc.) occupying the tetrahedral sites, and trivalent metal cations (such as Fe³⁺) occupy the octahedral sites. In case, if all divalent metal ions are filled by the octahedral site, and the trivalent metal cations are partially in both the tetrahedral and octahedral sites are known as inverse spinel ferrites.

Various techniques and methods have been used to get a desired spinel ferrite material, in order to fulfil the specific requirements. Spinel ferrite-based thin films have the potential for miniaturization of modern technology devices in electronic industries, energy storage fields, and information technology as, switching devices, lithium-ion batteries [10], supercapacitors [11], magnetic sensors [12], data storage devices [6], etc. Many researchers have worked

on different metal ions such as Co, Ni, Mn, Mg, Cu, etc. based on spinel ferrite material. Among them, CoFe_2O_4 thin films have attracted considerable attention owing to their superior inherent properties. CoFe_2O_4 thin films have been fabricated by using various methods, such as thermal/electron beam evaporation system, spray pyrolysis, sol-gel, deep coating, sputtering, and molecular beam epitaxy. These methods require a specific substrate during film formation. Additionally, they also require expensive equipment and consume a lot of time to formation of the film. Here, we fabricate the thin films at a low cost with a self-devised method where the film can be formed in a very short span of time. In this work, free-standing, transferable CoFe_2O_4 thin films, offering enhanced flexibility for integration into various substrates have been formed. These films have been investigated for their structural and morphological properties.

Experimental Method

To formation CoFe_2O_4 thin films, 0.4 g of PVA was dissolved in distilled water for 1hr at 80 °C. Subsequently, a stoichiometric amount of FeCl_3 and CoCl_2 were also added to the PVA solution. The solution was stirred for the next 1 hr, which resulted in a transparent solution. After cooling the solution, a stoichiometric amount of solution was taken in a petri dish and placed inside the film formation chamber. Inside the chamber, a magnetic field on 1 tesla was applied to the petri dish. In order to form the film on the surface of the solution, a measured volume of NH_3 vapours was purged inside the reaction chamber, which was then kept closed for 15 minutes. The NH_3 vapours get react with the surface of the precursor solution which converted into a solid floating film. After formation, the film was taken on a glass substrate, which was sintered at 300 °C for 1 hour and investigated for structural and morphological properties.

Results and Discussion

XRD analysis

Figure 1(a) and (b) show XRD patterns of CoFe_2O_4 thin films prepared without and with external magnetic field applied in a normal direction to the surface of the solution, respectively. The film formed in the absence of magnetic field exhibits diffraction peaks at 2θ values of 18.5, 31.5, 35.6, and 43.7, corresponding to their (111), (220), (311), and (400) planes, respectively. These observed peaks are well matched with JCPDS card number 22-1086, confirming the cubic crystalline structure. The XRD pattern of the film fabricated with a normal to plane magnetic field is shown in figure 1(b), exhibits a single diffraction peak at angle 2θ corresponds to the plane (220). The specific orientation shows that the external magnetic field applied during film formation causes the crystallites within the film

and aligns in a unidirectional manner, resulting in a preferred orientation along the plane (220).

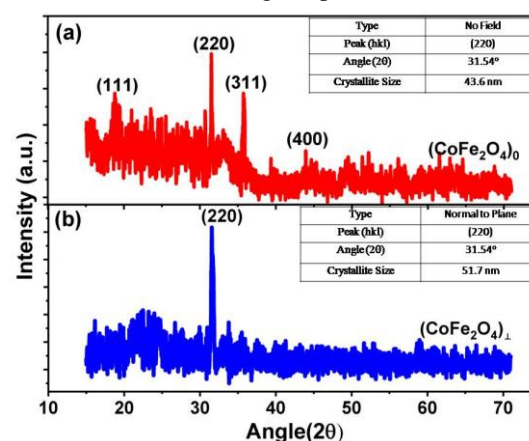


Figure 1: XRD pattern of CoFe_2O_4 thin films: **a.** XRD pattern of the film formed without applying magnetic field and **b** formed in the normal to plane direction of magnetic field during film formation.

The crystallite size of CoFe_2O_4 thin films is determined by using the Scherrer formula[13] represented as:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where D denotes the crystallite size in nanometer (nm), λ signifies the X-ray wavelength (1.54 Å), k represents the shape factor ($k=0.9$), θ indicates diffraction angle in degrees and β refers to the peak broadening at half of the maximum intensity of (220) diffraction peak. Scherrer's equation assumes spherical nanoparticle shapes, which may limit its accuracy when applied to non-spherical or irregularly shaped nanoparticles, as in the case of our thin films spherical nanoparticles. The average crystallite size is found to be 43.6 nm for the film formed without application of magnetic field, which increased to 51.7 nm in the presence of external magnetic field. The lattice constant in case of no magnetic field is 8.02 Å, which changed to 8.00 Å in the magnetic field. The slight reduction in the lattice constant under an external magnetic field is likely due to the directional arrangement of cations, leading to increased order and compactness, thereby causing minor lattice contraction.

FE-SEM analysis

Figure 2(a) displays the surface morphology of the CoFe_2O_4 thin film. The spherical-shaped nanoparticles can be seen uniformly distributed across the surface indicating a compact and homogeneous structure. In the figure 2(b), a cross-sectional FE-SEM image of the film, shows a dense layer without voids inside the film. The film possesses a uniform thickness of 152 nm, resulting from a precise control over the formation of thin film, revealing its structural homogeneity. Thus, the film exhibits a dense formation.

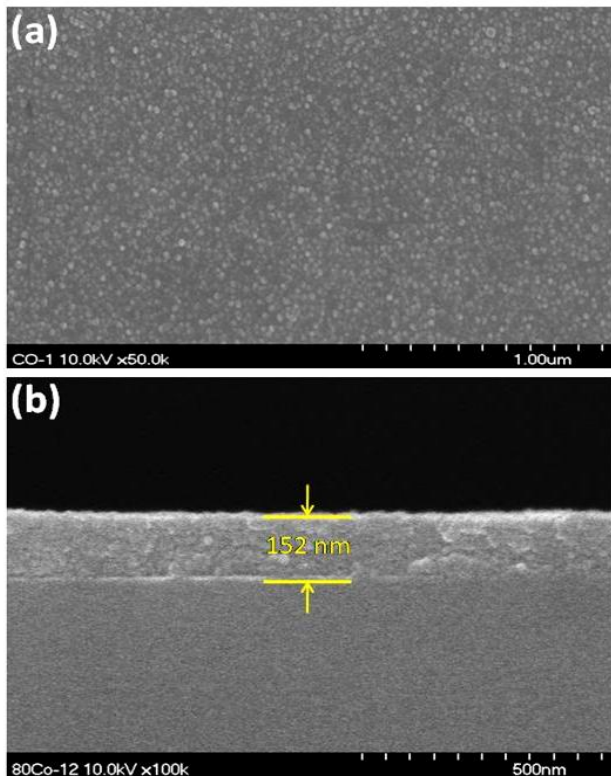


Figure 2: FE-SEM images of CoFe_2O_4 thin film: **a.** displays a top surface morphology, and **b.** shows cross-sectional surface of the film.

FTIR analysis

The examination of organic, inorganic functional groups and bonds formed in CoFe_2O_4 thin film analysed by the FTIR are shown in figure 3. The band arises around 495 cm^{-1} to 580 cm^{-1} corresponds to the stretching vibration of Fe-O metal ion bonds in the tetrahedral sites (Fe^{3+}). Similarly, the lower frequency band between 410 cm^{-1} and 485 cm^{-1} is attributed to the stretching vibration of Co-O metal-oxygen bond in the octahedral sites (Co^{2+}).

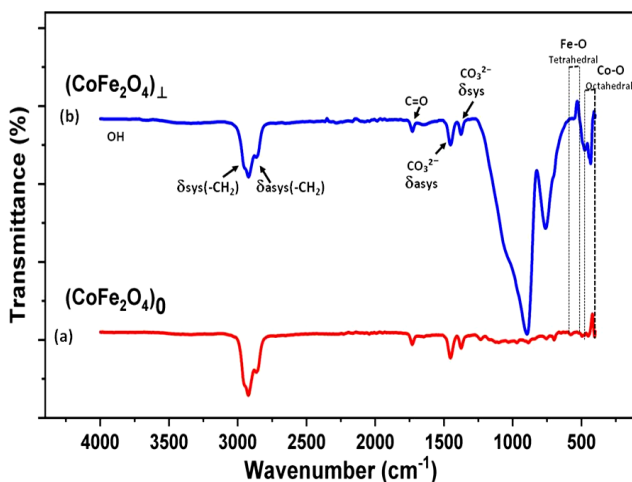


Figure 3: FTIR spectra of CoFe_2O_4 thin films: **a.** Spectra of the film formed without applying magnetic field and **b** formed in the normal to plane direction of magnetic field during film formation.

Graph 3(a) represents the lower intensity at a lower wave number of CoFe_2O_4 film spectra, fabricated without applying magnetic field during formation. When external magnetic field is applied, it influences the orientation of Fe^{3+} and Co^{2+} cations within the tetrahedral and octahedral sites, leading to enhanced band intensity and improved structural stability at lower wave numbers. Additionally, the bands observed at 1375 cm^{-1} , 1451 cm^{-1} , 1734 cm^{-1} indicate the presence of symmetric and asymmetric stretching vibrations of carbonate (CO_3^{2-}) groups as well as carbonyl stretching vibrations ($\text{C}=\text{O}$) at surface of the film. These bands may result from surface contaminations such as the existence of carbonation on the surface of films as a result of the adsorption of atmospheric CO_2 and reacting with residual hydroxyl groups. Furthermore, the carbonyl vibrations indicate oxidation by-products or organic residues may form during the films formation process. The bands arise at 2862 cm^{-1} , 2931 cm^{-1} , and 3660 cm^{-1} suggesting the presence of symmetric, asymmetric stretching vibrations of hydrocarbon and O-H stretching, from adsorbed water molecules on the surface of the film. These surface contaminants slightly change the chemical composition and affect its functional properties. From the FTIR spectra, these bands are the evidences of the formation of CoFe_2O_4 films.

The ferromagnetic CoFe_2O_4 has an inverse spinel structure and is interesting because it has a high coercivity, high magneto crystalline anisotropy, and moderate saturation magnetization. The magnetic behaviour of freestanding CoFe_2O_4 thin films is expected to be influenced by the formation methods, particularly in the presence and absence of an external magnetic field during growth of the film. The films fabricated without an external magnetic field should have isotropic magnetic characteristics, owing to domains aligned randomly to reduce magnetostatic energy. Similarly, in the absence of a substrate, strain-induced anisotropy is expected to be eliminated, leaving magneto crystalline and shape anisotropy as the predominant factors. In case, the films are grown in an external magnetic field, the magnetic moments must be aligned along the magnetic field direction. Therefore, film grown in normal of magnetic field should have substantial perpendicular magnetic anisotropy.

Conclusion

CoFe_2O_4 films are formed without and with applying magnetic field successfully on the surface of glass substrate. XRD study confirms the formation of cubic spinel crystal structure of CoFe_2O_4 films. The average crystallite size of the films increases and lattice constant decreases with the

application of external magnetic field during formation. The FE-SEM reveals that the film consists of uniformly distributed, spherical grains forming a dense, continuous layer without discontinuities. FTIR spectroscopy confirms the presence of various functional groups and metal-oxygen cations associated with tetrahedral and octahedral sites of the as - formed CoFe_2O_4 films can be proposed for spintronic and magnetic storage applications.

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