Thickness Dependent Physical Property of Spray Deposited ZnFe₂O₄ Thin Film

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Abstract: Thin film of spinel ferrite has wide range of application such as magnetic sensor, reading head for magnetic recording media, switch mode power supplies, deflection yoke rings and spintronics devices. These wide applications are due to its high permeability, large resistivity, relatively high magnetization and low coercivity. In the present study spinel ZnFe₂O₄ with good adhesion on glass substrate have been prepared using home built spray pyrolysis unit from mixed zinc and iron nitrates of 1:2 M aqueous solutions. Photograph of the prepared film shows that as film thickness increases, the color of the film changes from golden yellow to red-brown and is due to increase in grain size. X-ray line broadening technique was adopted to obtain grain size and microstrain. It was observed that the surface morphology and optical transmittance strongly depends on film thickness. Band gap of the film varies from 2.08 to 2.70 eV as film thickness decreases. The effect of film thickness on crystalline nature, surface morphology and optical properties were analyzed and reported.

Key words: Spinel ferrite, ZnFe₂O₄ thin film, spray pyrolysis

INTRODUCTION

The spinel ferrite thin films are used for various applications such as in magnetic sensor, reading head for magnetic recording media, microwave devices, switch mode power supplies, deflection yoke rings and spintronics devices. These wide applications are due to its high permeability, large resistivity, relatively high magnetization and low coercivity. It can also absorb electromagnetic radiation in the microwave bands (Gupta et al., 2007) and can be used as a photocatalyst under visible light irradiation (Jang et al., 2009). The spinel type oxide is a cubic structure and consists of tetrahedral A oxygen sites and octahedral B oxygen sites in which metal cation distribution occurs. This spinel type oxide growth process involves the so-called Wagner's cation counter diffusion mechanism.

Among all spinel ferrite materials, ZnFe₂O₄ (Franklinite) has better potential application with its normal spinel structure. There are many techniques available for the synthesis of ZnFe₂O₄ thin films such as chemical vapour deposition, spin coating, thermal evaporation, spin spray ferrite plating, sputtering, Laser ablation techniques and spray pyrolysis. The technique of spray pyrolysis is simple and inexpensive for the preparation of homogeneous ZnFe₂O₄ thin films with a large surface area. In this study, spray deposited Zinc Ferrite thin film is prepared with different thickness and its correlation on physical property is analyzed and reported.

MATERIALS AND METHODS

Zinc ferrite thin films were grown on a glass substrate by spray pyrolysis technique. It was prepared by taking a 0.02 M aqueous solution of zinc nitrate and 0.04 M aqueous solution of ferric nitrate. The prepared solution was sprayed onto glass substrate at a temperature of 350°C. In order to obtain homogeneous oxide of the zinc ferrite thin films, prior to characterization, the films were annealed at 350°C for 5 h (Wu et al., 2001). To obtain thin films with different thickness the volume of the solutions was varied between 20 and 80 mL in step of 20 mL. The deposited zinc ferrite films were characterized for structural, optical and surface morphology for different thickness. X-ray diffraction measurements were used to examine the crystalline nature of the prepared films. CuKα, (λ = 1.54060 Å) was used in this study. Optical studies were carried out using a UV-Vis-NIR double-beam spectrophotometer (Model Lambda35) in the wavelength range between 250-1100 nm.

Structural studies: The X-ray diffraction of the zinc ferrite film deposited at 350°C with different thickness is shown in Fig. 1. The probability of crystallization

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Fig. 1: X-ray diffractograms of the zinc ferrite thin films

Fig. 2: Correlation between thickness, grain size, strain and lattice parameter

Fig. 3: Photo image of zinc ferrite film with different thickness, (a - 276 nm, b - 329 nm, c - 413 nm, d - 428 nm)

increases as the film thickness increases and the X-ray spectra are polycrystalline in nature (Gopalan et al., 2009). The various thickness of zinc ferrite film showed a preferred orientation of (311) peak at 35° (Wu et al., 2001) which are in good agreement with the reported standard values (JCPDS No. 22-1012). From Fig. 2, it indicates that the grain size increases due to the grain growth in thin film as the thickness increases. The strain in the film decreases from 0.002145 to 0.00065484 lines/m with increase in film thickness. This is due to the fact that the cohesive force between the film and the substrate decreases. The lattice parameter of ZnFe₂O₄ thin film is found to be wavy in nature from 8.373084613 to 8.398854788 Å.

Optical studies: The prepared film shows that as film thickness increases, the color of the film changes from golden yellow to red brown due to increase in grain size as shown in Fig. 3. The thickness of the film is measured by surface profilometer and is found to be varying from 276-428 nm. The optical absorbance spectra of ZnFe₂O₄
film with different thickness are shown in Fig. 3. The absorbance of the film shown in Fig. 4 increases with increase in film thickness because in thicker films more atoms are present so more states will be available for the photons to be absorbed. Figure 5 shows that the transmittance of the film varies from 85 to 55% with increase in film thickness. This is due to the phenomena that as the thickness increases the scattering of light increases so that the coherence between the primary light beam and the beam reflected between the film boundaries is lost resulting in disappearance of the interference with decrease in transmittance.

The variation of optical bandgap as a function of thickness is shown in Fig. 6. The optical bandgap of the film varies from 2.08 to 2.70 eV as film thickness decreases (Wu et al., 2001; Zhou et al., 2002). The grain size increase with increase in film thickness. Since the grain size influences the energy level of electrons, the band gap depends on the thickness of the film. This is due to the effect of quantum size seen in thin films of semiconductor. It is evident from the graph that the band gap widens towards blue shift with decrease in the thickness (Kislov et al., 2008). This kind of broadening effect can be studied based on Burstein effect (Burstein, 1954).

**Surface morphology:** The SEM image with different thickness is shown in Fig. 7. It is observed that the surface morphology depends on the thickness of the film. The grain size is found to be ranging from 20 to 30 nm in ZnFe$_2$O$_4$ film. The film with thickness of 276 nm shows grain nucleation sites. As the thickness increases to 329 nm the grain growth in the film increases. Further increase in film thickness of about 413 nm leads to layers growth of film. It is seen that the grain size increases and
Fig. 7(a-d): SEM image of ZnFe₂O₄ thin film with different thickness; (a) 276 nm, (b) 329 nm, (c) 413 nm and (d) 428 nm

Fig. 8(a-d): B-H curve of ZnFe₂O₄ thin film with different thickness; (a) 276 nm, (b) 329 nm, (c) 413 nm and (d) 428 nm
the crystallization increases with the film thickness (Tian et al., 2010). Thus the final film of thickness 428 nm is observed with larger grains of improved crystallization.

Magnetic studies: The first graph indicates diamagnetic nature which is due to the presence of zinc content in large amount as shown in Fig. 8. Then, the dip in the Curve represents the transition of diamagnetic nature to ferromagnetic nature of the material with increase in thickness as shown in Fig. 5. In soft magnetic materials, the domain walls moves easily back and forth resulting in easy magnetization and demagnetization. Thus the coercivity and retentivity decreases with increases in thickness of zinc ferrite film resulting in soft ferromagnetic material (Hofmann et al., 2004). Finally, Magnetic study reveals the enhancement of magnetic nature of the film as thickness increases.

CONCLUSION

Zinc ferrite thin films were prepared by spray deposition. With varying thickness the properties of thin films were studied. It had been observed that the films show spectacular shifts in physical properties with increase in thickness. The magnetic property of the film had shifted from diamagnetic nature to soft paramagnetic nature which finds many applications in high frequency devices. The crystallinity of the films increased with increase in thickness of the films. The study of optical properties reveals that the films can be best suited as gas sensors and for photocatalytic applications.

REFERENCES


