Fabrication and characterization of $\text{ZnFe}_2\text{O}_4$ thin film based metal-insulator-semiconductor capacitors

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**ABSTRACT**

Thin films of zinc ferrite ($\text{ZnFe}_2\text{O}_4$) were deposited on glass, quartz and p-silicon (100) substrates by the sol-gel method. The structural properties of the films were studied using x-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The XRD data show the film having a spinel structure and the crystalline phase exists after annealing at 500°C for 2 h in air. The SEM and AFM images show the nano-crystalline nature of the films. The optical transmittance decreased with increase of annealing temperature. The optical band gap energy was estimated at different annealing temperatures and found to be 2.71 eV after annealing at 400°C. The metal-insulator-semiconductor (MIS) capacitors were fabricated using $\text{ZnFe}_2\text{O}_4$ films on p-silicon (100) substrates. The capacitance-voltage (C-V), dissipation-voltage (D-V) and current-voltage (I-V) characteristics were studied. The dependence of dielectric constant on annealing temperature and signal frequency was analyzed. The variation of current density and resistivity of the $\text{ZnFe}_2\text{O}_4$ films with annealing temperature was also explored.

**1. INTRODUCTION**

Nowadays spinel ferrites have attracted many researchers due to their remarkable magnetic properties and applications in many areas, such as magnetic devices and switching devices [1], [2], gas sensors [3] and photo-catalysts [4], etc. Metal oxide thin films were deposited by various physical [5], [6] and chemical methods [7], [8]. $\text{ZnFe}_2\text{O}_4$ thin film or powder was prepared by various methods, including hydrothermal synthesis [9], co-precipitation method [10], and sol-gel method [11]. Sol-gel method is preferred because of its simplicity, cost effectiveness, room temperature deposition and elimination of the need for vacuum apparatus. Plocek et al. [12] reported the preparation of $\text{ZnFe}_2\text{O}_4$/SiO$_2$ nano-composites by the sol-gel method. Veith et al. [13] studied the synthesis of nano-crystalline $\text{ZnFe}_2\text{O}_4$ and zinc-iron oxide composites by the sol-gel method. Li et al. [14] reported the optical and structural properties of $\text{TiO}_2$-$\text{ZnFe}_2\text{O}_4$ composite film prepared by r.f. sputtering method. Khorrami et al. [15] reported the structural characterization of $\text{ZnFe}_2\text{O}_4$ nano-powders prepared by the sol-gel auto-combustion method. Hofmann et al. [16] studied the neutron diffraction patterns, temperature dependence of the magnetic moment and dc magnetic susceptibility etc. for the nano-structured $\text{ZnFe}_2\text{O}_4$. Bangale et al. [17] reported the synthesis of nanocrystalline $\text{ZnFe}_2\text{O}_4$ powder by novel self combustion method using urea as a fuel. They studied the thermal, structural, morphological and hydrophilic properties of $\text{ZnFe}_2\text{O}_4$.

In this paper, the preparation of spinel $\text{ZnFe}_2\text{O}_4$ films on glass, quartz and silicon substrates by the sol-gel method and the effect of annealing temperature on structural and electrical characterization of these films are reported.
2. EXPERIMENTAL PROCEDURE

ZnO [18] and Fe$_2$O$_3$ sols were prepared using zinc acetate dihydrate and ferric chloride hexahydrate as the precursor materials, respectively and 2-methoxy ethanol and deionized water were used as the solvents. Diethanol amine was added as a stabilizing agent. Zinc acetate dihydrate was first dissolved in a mixture of 2-methoxy ethanol and diethanolamine at room temperature. The concentration of zinc acetate was 0.5 M (A) and the molar ratio of diethanolamine to zinc acetate was kept as 1:1. The concentration of ferric chloride was also 0.5 M (B). The sols of ZnO (A) and Fe$_2$O$_3$ (B) were stirred separately for 2 h and then slowly mixed with one another and constantly stirred for 24 h for complete hydrolysis. The resultant sol of ZnFe$_2$O$_4$ (C) was stored in an air tight bottle as a stock solution. A few drops of the sol (C) were placed on pre-cleaned glass, quartz and silicon (100) substrates and spin coated at a speed of 3000 rpm and spinning time of 40 s. The films obtained were dried in air and subjected to annealing at different temperatures from 80°C to 800°C (on quartz and silicon substrates). The MIS capacitors were fabricated using ZnFe$_2$O$_4$ films on p-silicon (100) substrates. The schematic of MIS capacitor is shown in Fig. 1. The RCA cleaning procedure was reported earlier [19].

The structural studies were done using Philips x-ray diffractometer with monochromatic Cu-K$_\alpha$ radiation. The morphology of the film was studied using scanning electron microscopy (SEM) (Raith, eLiNE). The optical studies were performed using UV-VIS-NIR-Spectrophotometer (Ocean Optics, USA, Model: HR-4000). Capacitance–voltage, dissipation-voltage and current–voltage measurements were done using Agilent 4155C and 4284 LCR meter. The electrical parameters such as current density and electrical resistivity were measured from the I-V characteristics. The film thickness was measured by surface profilometer and envelope method [20].

3. RESULTS AND DISCUSSION

The XRD patterns of ZnFe$_2$O$_4$ film deposited on glass substrate annealed at 400°C and 500°C are shown in the Fig. 2. It can be seen from Fig. 2 that, the spinel structure of ZnFe$_2$O$_4$ is formed after the film annealed at 500°C for 2 h in air ambient. By increasing the annealing temperature above 500°C, well crystallized ZnFe$_2$O$_4$ can be obtained [11]. The peaks corresponding to (220) and (311) represent spinel type lattice structure. The XRD results are confirmed with SEM images.

![Fig. 1. MIS structure (Al/ZnFe$_2$O$_4$/p-Si) in a vertical MIS capacitor](image-url)
Fig. 2. XRD patterns of ZnFe$_2$O$_4$ film deposited on glass substrate annealed at (a) 400°C and (b) 500°C for 2 h in air.

Fig. 3 shows the SEM images of ZnFe$_2$O$_4$ films deposited on p-silicon (100) substrates annealed at 200, 400, 500 and 800°C for 2h in ambient air. The film annealed at 200°C showed featureless, amorphous nature, while the film annealed at 400°C showed the starting of the formation of grains. After annealing at 500°C, film showed well crystallized structure with grains of irregular, granular, spherical and rod-like structures. The grain size was in the range 400-900 nm. The grain size was increased with increase of annealing temperature due to the coalescence.

Fig. 4 shows the atomic force microscopy (AFM) image (3D view and surface morphology) of ZnFe$_2$O$_4$ film on silicon substrate annealed at 500°C for 2h. It has been observed that, the surface roughness was very high and the image surface roughness $R_{\text{max}}$ was found to be 446 nm. The film also showed highly porous morphology.
Fig. 3. SEM images of ZnFe$_2$O$_4$ film on silicon substrate annealed at (a) 200°C, (b) 400°C and (c) 500°C for 2 h in air.

Fig. 4. AFM images of ZnFe$_2$O$_4$ film annealed at 500°C for 2 h (a) 3D view (b) surface roughness analysis
Fig. 5. Capacitance-voltage plot of ZnFe$_2$O$_4$ film annealed at different temperatures for 2 h in air

Fig. 5 a, b, and c show the capacitance-voltage plot of ZnFe$_2$O$_4$ film on silicon annealed at 200, 400 and 500°C, respectively for 1h in air and the corresponding film thickness was found to be 126, 118 and 115 nm, respectively. The oxide capacitance and dielectric constant values at different signal frequencies are reported in Tab.1. It has been observed the dielectric constant decreased with increase of signal frequency. Also, the dielectric constant increased with increase of annealing temperature. The dependence of loss tangent (dissipation) with frequency and annealing temperature is shown in Fig.6. It is to be noted that, the loss tangent was minimum at the signal frequency of 500 kHz in all the three different cases. The loss tangent increased at higher signal
frequencies. The loss tangent was quite high at an annealing temperature of 200°C. The values are reported in the Table 1.

**Table 1.** Electrical parameters of ZnFe$_2$O$_4$ film annealed at different temperatures and signal frequencies

| Annealing temperature (°C) | Signal frequency (kHz) | Oxide capacitance ($10^{-10}$ F) | Dielectric constant | Loss tangent (δ) |
|---------------------------|------------------------|----------------------------------|---------------------|-----------------|
|                           |                        |                                  |                     |                 |
| 200                       | 100                    | 2.186                            | 5.617               | 0.668           |
|                           | 500                    | 1.301                            | 3.343               | 0.637           |
|                           | 1000                   | 1.006                            | 2.585               | 0.777           |
| 400                       | 100                    | 1.662                            | 4.00                | 0.413           |
|                           | 500                    | 1.520                            | 3.658               | 0.304           |
|                           | 1000                   | 1.367                            | 3.290               | 0.468           |
| 500                       | 100                    | 2.467                            | 5.780               | 0.403           |
|                           | 500                    | 2.143                            | 5.026               | 0.357           |
|                           | 1000                   | 1.872                            | 4.391               | 0.566           |

**Fig. 6.** Loss tangent-voltage plot of ZnFe$_2$O$_4$ film at different frequencies annealed at different temperatures for 2 h in air.
Fig. 7. I-V characteristics of ZnFe$_2$O$_4$ film annealed at different temperatures for 2 h in air.

Fig. 7 a, b and c show the I-V characteristics of ZnFe$_2$O$_4$ film annealed at 200, 400 and 500$^\circ$C, respectively for 2 h in air. It is clear from the figure that, the variation of current with gate voltage is non-linear for the film annealed at 200 and 400$^\circ$C, which show rectifying nature, while the film annealed at 500$^\circ$C, showed almost linear dependence which depicts ohmic nature. The current density values of the film annealed at 200, 400 and 500$^\circ$C are found to be 2.00x10$^{-6}$ Acm$^{-2}$, 2.09x10$^{-6}$ Acm$^{-2}$ and 2.72x10$^{-5}$ Acm$^{-2}$, respectively. The resistivity values calculated for the film annealed at 200, 400 and 500$^\circ$C were found to be 1.981x10$^{11}$ Ωcm, 2.023x10$^{11}$ Ωcm and 1.595x10$^{10}$ Ωcm, respectively. It has been observed that, the current density increased at an annealing temperature of 500$^\circ$C, while the resistivity decreased at the same temperature.

4. CONCLUSION

In summary, spinel ZnFe$_2$O$_4$ thin films were synthesized by the sol-gel route. MIS capacitors were designed using ZnFe$_2$O$_4$ thin films as insulating layers. The dependence of dielectric constant and loss tangent on annealing temperature and frequency was investigated. Because of high resistivity and low leakage current, the ZnFe$_2$O$_4$ films may be used as gate insulators in CMOS applications.
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