γ-Fe$_2$O$_3$ to Fe$_3$O$_4$ phase Transition in Microwave based Sol-Gel Synthesis of Iron Oxide Thin Films – Role of Aluminum Doping

* Sidra Khalid$^{1)}$, Aseya Akbar$^{1)}$, Saira Riaz$^{2)}$ and Shahzad Naseem$^{2)}$

$^{1), 2)}$ Centre of Excellence in Solid State Physics, Punjab University, Lahore, Pakistan

*sidra.khalid@umt.edu.pk

ABSTRACT

Doped thin films of iron oxide have attracted widespread interest in recent years by virtue of their unusual magnetic and electronic applications in magnetic random access memories, spin transistors, data storage devices. Three important crystallographic phases of iron oxide include maghemite (γ-Fe$_2$O$_3$), hematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$). Among these iron oxide phases, maghemite and magnetite are of particular importance due to their magnetic moment. Electronic and magnetic properties of iron oxide thin films can enhanced/tuned using doping strategies. Aluminum doped iron oxide thin films are prepared using microwave assisted sol-gel route with fixed microwave intensity of 72% and dopant concentration of 0.02, 0.04, 0.06, and 0.08. XRD results confirm presence of maghemite phase in undoped thin films of iron oxide. As dopant atoms occupy the space available on the cationic sublattice transition from maghemite to magnetite phase is observed at high dopant concentration of 0.06. With further increment in concentration to 0.08 diffraction peak intensity increases exhibiting strengthening and increased crystallinity of the films. High dielectric constant of magnetite thin films 135.47(log f = 5.0; dopant concentration 0.08) arises due to formation of magnetite phase. Changes in dopant concentration and phases results in changes in grain boundary resistance and relaxation time thus affecting the dielectric properties.

1. INTRODUCTION

During the last few decades, iron oxide also known as half metal has vast applications in spintronics like spin field effect transistors and magnetic tunnel junctions [MJT] (Shen et.al 2012, Ziese and Thornton 2000). Iron oxide has three most important polymorphs as maghemite (γ-Fe$_2$O$_3$), hematite (α-Fe$_2$O$_3$) and magnetite Fe$_3$O$_4$ (Bourgeois et al. 2013). Fe$_3$O$_4$ is an important class of material exhibit unique magnetic, magneto- optical and magneto-resistive properties (Tabis et al. 2013). One of the important features of iron oxide thin films is the versatile nature that allow variation in composition / doping of different elements or by changing crystal morphology (Mornet et al. 2006)

Magnetite has more advantages in comparison to other iron oxide phases. It is a half metal with 100 % spin polarization and at room temperature, it acts as a conductor. Its conductivity occurs due to chances of electron hoping between Fe$^{3+}$ and Fe$^{2+}$
cations present on octahedral sites. Magnetite and maghemite both have ferrimagnetic behavior because of two cationic sublattices presence but due to the vacancies present in maghemite, reduction of magnetic moment occurs as compare to that of magnetite. Hematite has somewhat different corundum structure and magnetic properties. It shows hexagonal corundum strucure with weak ferromagnetic or antiferromagnetic behavior (Zajak et al. 2011)

Magnetite magnetic properties can be enhanced by doping of different elements, include Cr, Co, Zn etc., as reported in literature. These enhancements depend on valence state and ionic radius of these elements. Al\(^{3+}\) falls in the category of trivalent cations. It is preferred due to its close ionic radius value (0.675Å) to that of Fe\(^{3+}\) (0.69Å) ionic radii. Very little attention is given to aluminium doped iron oxide thin films especially regarding to their magnetic properties. However preparation of phase pure magnetite is very difficult despite of above advantages (Riaz et al. 2014). Since oxidation of magnetite easily occurs thus results in conversion of magnetite phase to maghemite. These methods utilize long reaction time and high temperature. These problems have been diminished by using sol-gel route assisted by microwave. Major challenge is to synthesize protocols by economic method. Modern preparation methods must produce high yields and high purities at less energy consumption. In this way, use of microwave shows promising behavior and has currently applied for the formation of thin films of iron oxide by many researchers. By using microwave, reaction time for the preparation of thin films becomes very less i.e. in minutes (Matusuzuki et al. 2013). Use of microwave energy results in direct volumetric, which reduces wall effects and gives homogeneous heating uniform crystal size, high crystallinity of thin films is dependent on the homogeneity of reaction so microwave is an efficient heating tool. Also frequency of microwave plays an important role for phase pure iron oxide thin films ranging from 0.3- 30 GHz. Microwave has alternating electromagnetic fields co-relate inside the material. These interactions results orientation of polar molecules in the applied field direction, when field direction is in opposite way molecules try to reorient themselves in the reverse field direction evolve heat through molecular friction. Relaxation and / or resonance are two major processes to transfer energy between material and microwave (Matusuzuki et al. 2013).

In this research work, un-doped and Al doped thin films of iron oxide using microwave intensity of 72% and dopant concentration is varied as 0.02, 0.04, 0.06, and 0.08. Structural, dielectric, magnetic properties have been interlinked with the change in dopant concentration.

2. EXPERIMENTAL DETAILS

Synthesis of un-doped and doped (aluminum) thin films of iron oxide were carried out through microwave-based sol-gel route. Nitrate of iron was used as precursor and deionized water (DI H\(_2\)O) as solvent. Ethylene glycol (EG) was mixed in solution and stirred at room temperature for duration of 30mins. Sols were then subjected to microwave power of 72%. For doped (aluminum) iron oxide sol synthesis, DI water was used to dissolve nitrate of aluminum and added to iron oxide sol. Variation of dopant concentration was as 0.02, 0.04, 0.06, and 0.08.

Aging of sol was done at room temperature and copper substrate was used to deposit thin films. Etching of substrate was done with diluted HCl and in IPA and
acetone, ultrasonically agitation occurred. Spin coating of sol was carried at 3000rpm for duration of 30sec then it was dried and aged at room temperature. Annealing of films was done in vacuum at 300°C under 500Oe applied magnetic field for 60 mins.

Bruker D8 Advance X-ray Diffractometer was used for structural characterization and Hitachi S-3400N Scanning Electron Microscope was used for morphological properties. Magnetic properties were carried out using Lakeshore’s 7407 Vibrating Sample Magnetometer. 6500B impedance analyzer was used for dielectric properties.

3. RESULTS AND DISCUSSION

Fig.1 show X-ray Diffraction analysis for undoped and aluminum (Al) doped iron oxide thin films. Peaks of diffraction corresponding to (400), (330), (320) planes indicates the existence of pure maghemite phase (Fig.1 (a)) at dopant concentration 2%. By varying the dopant concentration from 0.02 to 0.04, maghemite phase of iron oxide is obtained (Fig 1(a-b)). However, diffraction peak intensity (400) reduces as doped Al occupy the vacancies on the cationic sublattices. Phase transition from maghemite to magnetite was observed at dopant concentration of 0.06 (Fig.1 (c)) exhibiting that dopant is well incorporated in the host lattice. As dopant concentration is increased to 0.08, the film crystallinity increases indicated by increase in peak intensities (Fig.1(d)). At dopant concentration of 0.08 the strengthening of magnetite phase is observed as peak corresponding to plane (422) emerged with high intensity.

Fig. 1 XRD patterns for aluminum doped iron oxide thin films with dopant concentration (a) 0.02; (b) 0.04; (c) 0.06; (d) 0.08 (*Fe$_3$O$_4$; $\gamma$-Fe$_2$O$_3$)

The crystallite size plot versus dopant concentration plot is shown in Fig. 2 (a). The crystallite size decreases as dopant concentration is increased to 0.02 to 0.04.
Further increase the dopant concentration to 0.08, crystallite size increases due to pure phase formation of magnetite. Localized heating effect generates around the ions by adding Al content in iron oxide that take active part in replacement process of comparable $\text{Al}^{3+}$ ionic radius with $\text{Fe}^{3+}$ cations. This localized heating and temperature gradient slightly stops the Ostwald ripening mechanism and initially decreases the crystallite size (Khan et al. 2015). As ionic radii of Al is comparable to iron that’s why further increase in dopant concentration increases the crystallite size.

Dislocation density increases as there is decrease in crystallite size by the variation in dopant concentration from 0.02 to 0.04 in Fig. 2 (b). Formation of maghemite phase cause distortion in the structure and high dislocation density was noticed. With increase in dopant concentration to 0.06, there is a sharp decrease in dislocation density because of phase transformation from maghemite to magnetite. Further increase in dopant concentration causes slightly decrease in dislocation density and then again increase.

Variation in strain versus dopant concentration plot is shown in Fig. 2 (c). High dislocation density gives high strain and vice versa. As the dopant concentration increases, strain increases first and then decreases due to the decrease contribution of maghemite phase.
Fig. 2 (a) Crystallite size (b) Dislocation density (c) Strain for aluminum doped iron oxide thin films

Unit cell volume of iron oxide thin films is drawn as a function of dopant concentration as shown in Fig. 3. Remarkable density increase results decrease in the unit cell volume. High values of unit cell volume resulted decrease in density of the films. The increase of unit cell volume is because of the decrease in dislocation density with replacement of Al$^{3+}$ with Fe$^{3+}$.

![Unit cell volume vs Dopant Concentration](image)

Fig. 3 Lattice parameters for iron oxide thin films

Room temperature magnetic measurements of aluminum doped iron oxide thin films are performed and M-H curves are shown in Fig. 4. In case of un-doped Fe$_2$O$_3$ thin films, because of difference in magnetization of two sublattices net magnetization occurs. However, random sublattices moments increases the net magnetic moments as there is increase in dopant concentration thus results in higher saturation magnetization.

![M-H Curves](image)
Mₘ increases with increase of carrier concentration from 0.2 to 0.4. More increase in saturation magnetization take place at 0.08 dopant concentration due to presence of pure magnetite phase. In Fe₂O₃ lattice, imbalance occurred due to presence of aluminum in host lattice, canting of spin structure. As the dopant concentration was varied beyond 0.08, increase in dislocations and more defects leads to random alignment of spins. This revealed decrease in saturation magnetization with less spin canting.

Dielectric constant and tangent loss versus frequency plot is shown in Fig. 6. By increasing frequency, dielectric constant decreases and at higher frequency it becomes constant shows normal dispersion behavior for all concentrations (0.02-0.08). Time needed by carriers to align in the field direction is the dispersion in dielectric. At high frequency carriers do not find enough time to make arrangement in the field direction (Nasir et al. 2014). Two layer Maxwell-Wagner model according to that specimen is comprised of grains and grain boundaries. It explains dielectric tangent loss as a function of frequency. Grains exhibit low resistivity values and high resistivity is shown by grain boundaries (Nasir et al. 2011). With the increase in frequency, there is a decrease of tangent loss. At low frequency more active grain boundaries occurs and at high frequency grains are more active.
Fig. 6 Dielectric constant for aluminum doped iron oxide thin films

The dielectric constant and tangent versus dopant concentration plots are shown in Fig. 7. As the dopant concentration is varied from 0.02 to 0.04, dielectric constant decreases due to low grain boundary. As the dopant concentration is varied from 0.04 to 0.08, there is a sharp increase in dielectric constant due to phase changes from maghemite to magnetite and high grain boundary resistance. As the dopant concentration is varied beyond 0.08, there is decrease in dielectric constant. This behavior is due to presence of oxygen vacancies and Fe$^{3+}$ cations displacement (Riaz et al. 2014).

Fig. 7 Dielectric constant as function of carrier concentration

4. CONCLUSIONS

Aluminium doped iron oxide thin films were synthesized using microwave intensity of 72% with dopant concentration 0.02, 0.04, 0.06 and 0.08. XRD results exhibited the presence of maghemite phase in un-doped aluminum oxide while by changing concentration from 0.02 to 0.04, maghemite phase persists. Transition to magnetite phase took place at dopant concentration 0.06 due to reason that into the host lattice, dopant has well incorporated. High dielectric constant and high saturation magnetization was observed for magnetite phase at dopant concentration 0.08. Real and imaginary impedance results revealed that change in dopant concentration strongly influence dielectric relaxation process.

REFERENCES


