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RESEARCH

Microstructure and magnetic properties of Ni-Zn ferrite thin film synthesized using sol-gel and spin-coating technique

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Abstract The nanocrystalline Ni-Zn ferrite thin film with the chemical formula $Ni_{0.3}Zn_{0.7}Fe_2O_4$ were deposited on glass substrate using sol-gel synthesis of metal nitrate aqueous solutions and spin-coating technique. Thin films of nickel-zinc ferrite have been prepared using spin-coating technique onto the ITO glass substrates. As-deposited films are annealed at 400, 500, 600 and 700 °C for 1 h. The Ni-Zn ferrite thin film with crystallite size of 20 nm has been successfully synthesized. The thickness of deposited films was below 300 nm and crystallite size was below 20 nm. The X-ray diffraction (XRD) analysis found the Ni-Zn thin films nanoferrite has a spinel cubic structure and lattice parameter of *Fd3m*. The crystallinity of the prepared Ni-Zn ferrite films increases as increase substrate temperature of a film deposition. Microstructures and chemical analysis by scanning electron microscopy and energy-dispersive spectroscopy showed that nanosized nickel-zinc ferrite particles with a diameter of 18.6 to 41.3 nm exist in the thin film. Magnetic properties of the Ni-Zn films have been characterised at room temperature, whereas the saturation magnetization M_s of the Ni-Zn films increase with increasing grain sizes. Maximum saturation magnetization M_s and coercivity H_c are 3.42 emu/g and 16.54 Oe for thin films annealed at 500 and 700 °C, respectively. The M_s of the films shows a trend increasing and the H_c value decreasing as increase the annealed temperature and the grain size of the Ni-Zn ferrite thin films. The conductivity decreases with increasing annealed temperature. It has been shown that the DC resistivity, saturation magnetization and coercivity of deposited films are influenced by annealing temperatures. The magnetic properties of Ni-Zn thin film with grain size of 18.6–41.3 nm shown a superparamagnetic behaviour were observed.

Keywords Ni-Zn ferrite thin film · Magnetic properties · Microstructure · Sol-gel · Spin-coating

Introduction

The demand for advanced technology in electronics has attracted research interest on the structural, magnetic and electrical properties of ferrites. The trend for downsizing electronic devices and the potential applications of soft ferrite materials have leads to the fabrication of ferrite thin films. Recent years, an impressive research work on the growth and characterization of ferrite thin film has been developed in the literature due to their wide range of technological application in numerous fields.

Ferrite thin films are very important for the fabrication of sensors [1], memory [2] and microwave devices [3]. There are several physical methods ion sputtering [2, 4, 5], pulsed laser deposition [6], sol-gel [7, 8] and spray pyrolysis [9–12], and chemical methods (solvothermal, photochemical, electrochemical, thermolytic, sol-gel, etc.) to synthesize nanocrystalline thin film and to control its crystal size [11]. Nickel ferrite is the most suitable material for device application. It has a technological importance in electrical and magnetic industries gas sensor material [12]. Sol-gel is a chemical method that fabricates material through the process of phase change from liquid phase (sol) to solid phase (gel). Fabrication that employs this method will usually be entailed by either spin-

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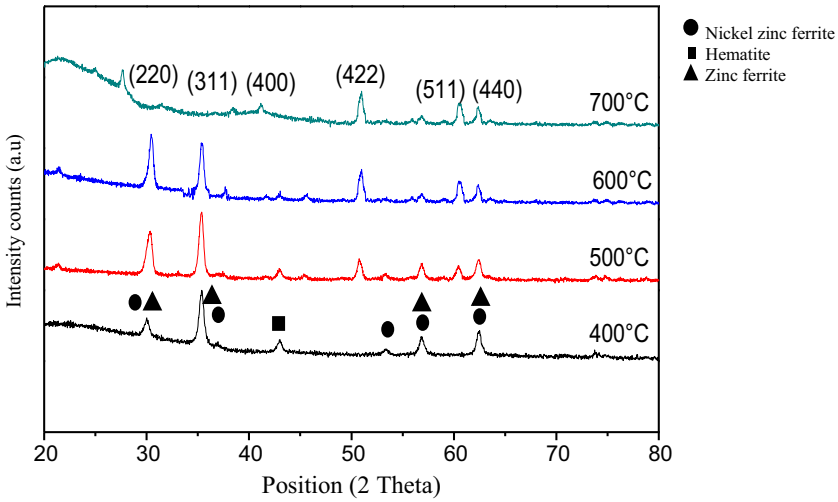

Fig. 1 XRD pattern of air annealed $Ni_{0.3}Zn_{0.7}Fe_2O_4$ thin films

coating or dip-coating process followed by heat treatment process. Walker et al. [13] found that annealing treatment is required to reduce material defects. Annealing treatment is a common procedure in fabrication of nanomaterial to either improve the quality of crystal or stabilize the structure at a temperature [14]. Wang et al. [15] studied the effects of annealing temperature on the structural and magnetic properties of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ thin films at room temperature. The coercivity were decrease as average grain size increased by varying the annealing temperature from 600 to 900 °C, while their saturation magnetization increased and the crystallinity improved as increase the annealing temperature. These results also agreed with Mathe and Bhosale [16].

A spin coating with a simple apparatus is a versatile technique for producing various thin film materials of a wide range of the composition in air at a relatively low temperature and a high deposition rate. The spin coating of Co ferrite films [17], Zn ferrite thin film [18] and Ni-Zn ferrite thin films [19] have been reported. In this work, nanostructured $Ni_{0.3}Zn_{0.7}Fe_2O_4$ ferrite thin films have been prepared by using sol-gel spin-coating method annealed at low temperatures (400–700 °C). As a result, the size of grains was obtained below 50 nm with annealing temperature at lower temperatures (400–700 °C) for crystallization. Using sol-gel synthesis route is useful to achieve the nanosize grains fabrication of magnetic ferrite thin films at relatively low annealing temperature. This sol-gel synthesis route is an efficient method to fabricate an integrated thin film device. The phase structure, magnetic hysteresis at room temperature, microstructure and conductivity of the nanostructure Ni-Zn nanoferrite thin films has been studied.

Experimental

The starting materials used were nickel nitrate hexahydrate, iron nitrate nanohydrate and zinc nitrate hexahydrate were used as a precursor for the starting sol preparation. The precursors were dissolved in a beaker using deionised water and

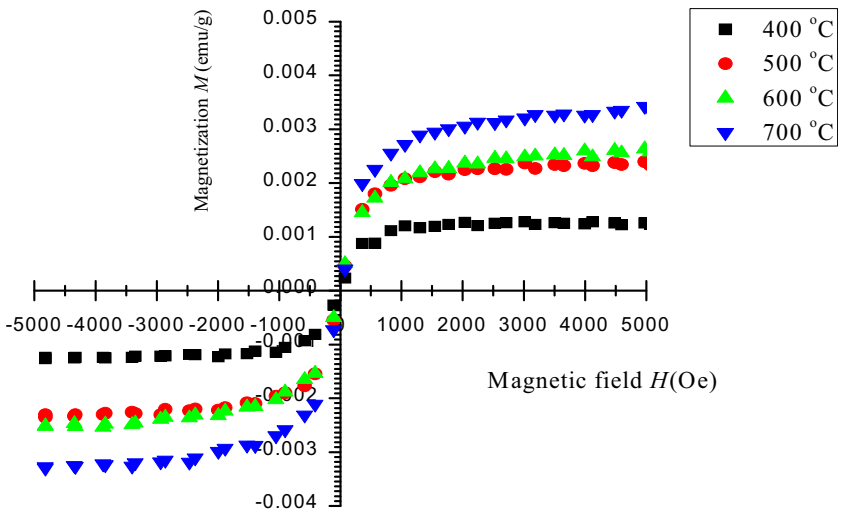

Fig. 2 Hysteresis loop of $Ni_{0.7}Zn_{0.3}Fe_2O$ ferrite thin films

Table 1 Saturation magnetization and coercivity of $Ni_{0.3}Zn_{0.7}Fe_2O_4$ ferrite thin films

Temp (°C)	M_s (emu/g)	H_c (Oe)	Grain size (nm)	Crystallite size (nm)
400	1.287	16.184	18.6	16.71
500	2.395	16.536	26.3	16.22
600	2.653	12.288	28.1	17.03
700	3.421	8.297	42.32	18.45

Table 2 Average grain size and thickness for different annealing temperature

Annealing temperature (°C)	400	500	600	700
Average grain size (nm)	18.61	26.25	28.12	41.32
Thickness (nm)	145.7	180.7	221.5	285.6

stirred for 15 mins with a molar ratio of Ni:Zn:Fe = 1:1:2 using a hot plate. A sol-gel formed after left 24 h for aged. The aged sol 1.0 ml was dropped on ITO glass substrate and spin coated for 25 s at 3500 rpm (revolutions per mins). The deposition was repeated several times to obtain the require thickness (300 nm). The films were drying in room temperature and annealed in air at temperatures of 400, 500, 600 and 700 °C. The structure and phase deposited films were examined by XRD using Philips X'pert diffractometer model 7602 EA Almelo operating at 40 kV/30 mA obtained in the theta range

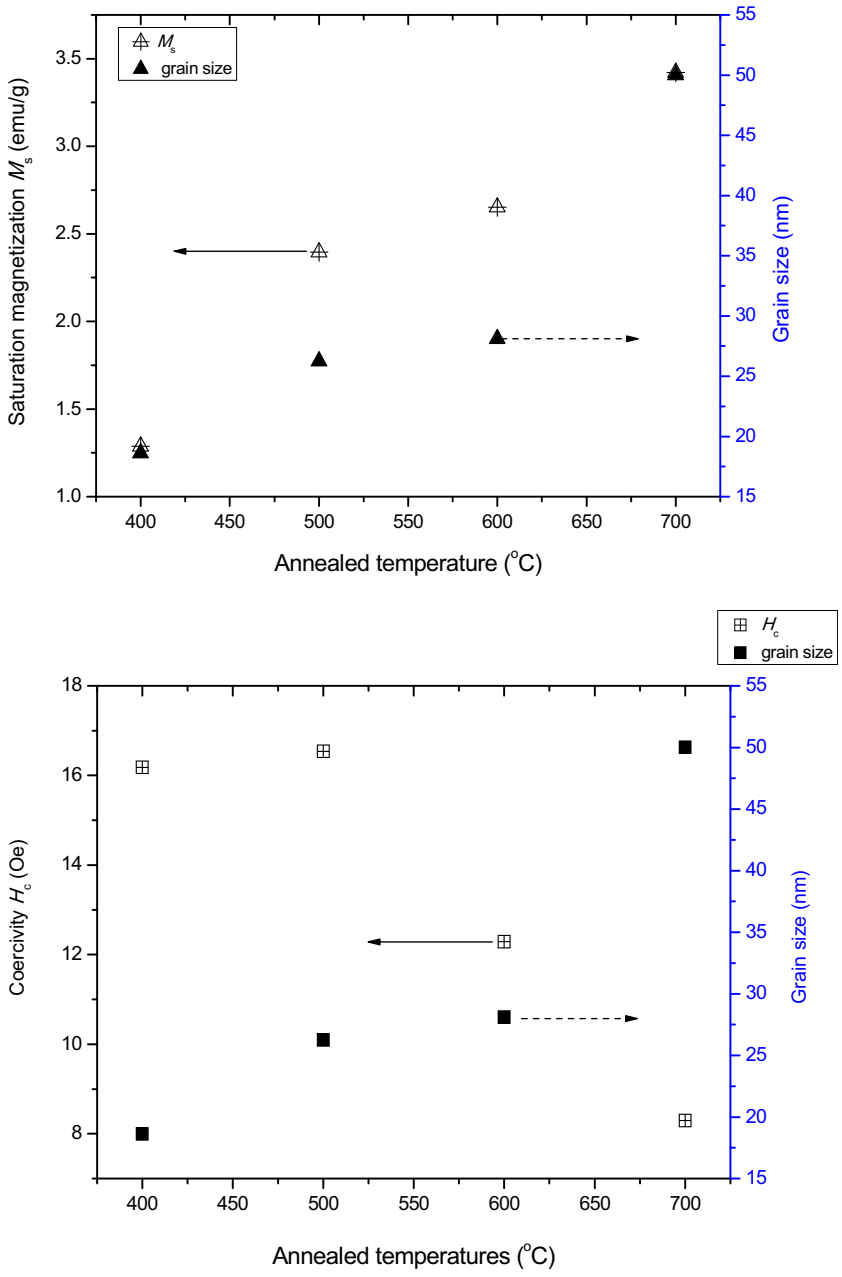

Fig. 3 Comparison of the variation in **a** saturation magnetization, and **b** coercivity and against the annealed temperatures, correspond to the grain size of the $Ni_{0.7}Zn_{0.3}Fe_2O$ ferrite thin films

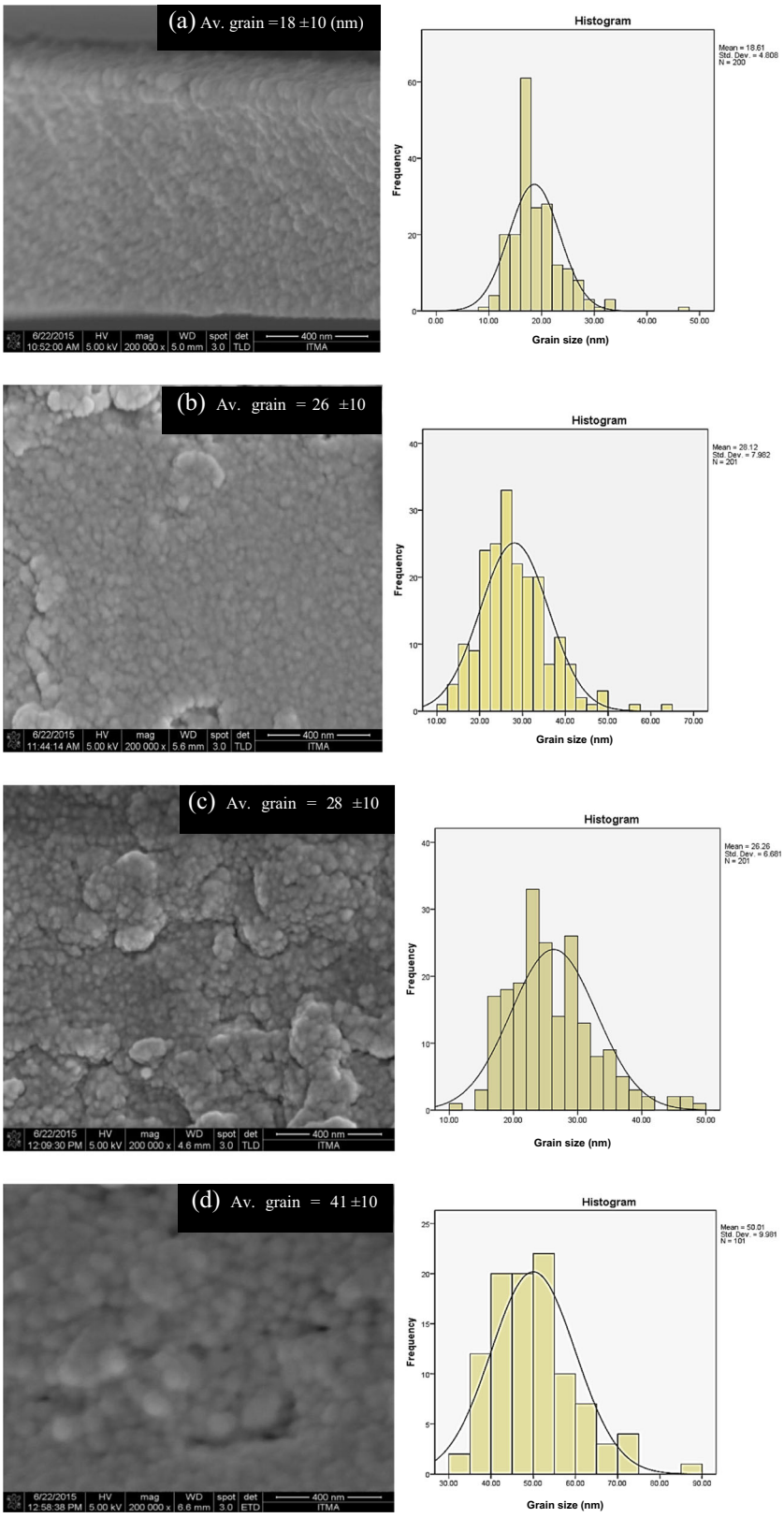

Fig. 4 FESEM images of the $Ni_{0.7}Zn_{0.3}Fe_2O$ ferrite thin films at **a** as-deposited, annealed at **b** 400, **c** 500, **d** 600 and **e** 700 °C

20° to 80° using low scan with 0.012° step size, 0.44 s scan step size, CuKα radiation ($\lambda = 1.5417$ Å). Magnetic properties of the samples; saturation magnetization (M_s), remnance magnetization (M_r) and coercivity (H_c) were recorded at room temperature using a vibrating sample magnetometer (VSM) model 7404 Lake Shore. The maximum value of the applied

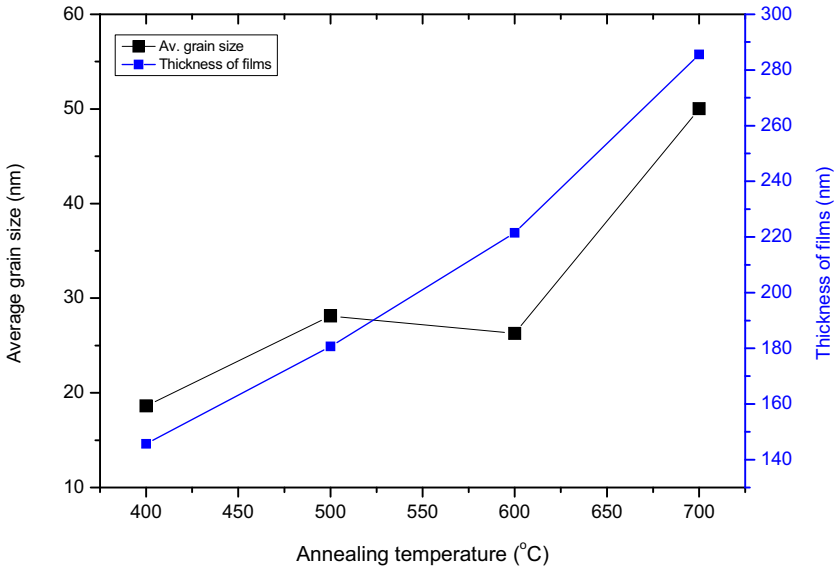

Fig. 5 The relationship of the average grain size and the films thickness

magnetic field is 5000 G (G), using an interval of 134 G. The microstructure and composition of the sample was carried out by a NovaNano 230 field emission electron microscopy (FESEM), voltage 5.0 kV with attached energy-dispersive (EDX) spectroscopy. The electrical resistance measurements were made by using standard two-probe method Keithley digital multimetres.

Results and discussion

Structural analysis

Figure 1 shows the XRD pattern of spin coating and air annealed ferrite thin films on the ITO glass substrate. The XRD patterns show single cubic spinel phase of the $Ni_{0.3}Zn_{0.7}Fe_2O_4$ ferrite thin films according to JCPDS reference code 74–2081 and 82–1049, respectively. As the increase in grain size as increasing annealing temperature, as indicate the narrowing the XRD spectrum lines. As (220), (311), (400), (511), (440) which are allowed peaks of the single cubic spinel structures. Plane (311) most intense in each annealing temperature whereas other at relatively low intense. These planes formed nickel–zinc ferrite phases. The small peak intensities in XRD pattern revealed the existence of fine grain nanocrystalline with the most part as amorphous. The crystallite sizes of all ferrite thin films are found to be between 16 and 18 nm calculated using Scherrer equation. Annealing temperature has pronounced the effect on grain size. The lattice parameter calculated for pure nickel ferrite thin film is 8.338 Å claimed by Gupta et al. [20]. This is in accordance with the variation in lattice parameter with Zn content reported for the bulk ferrites.

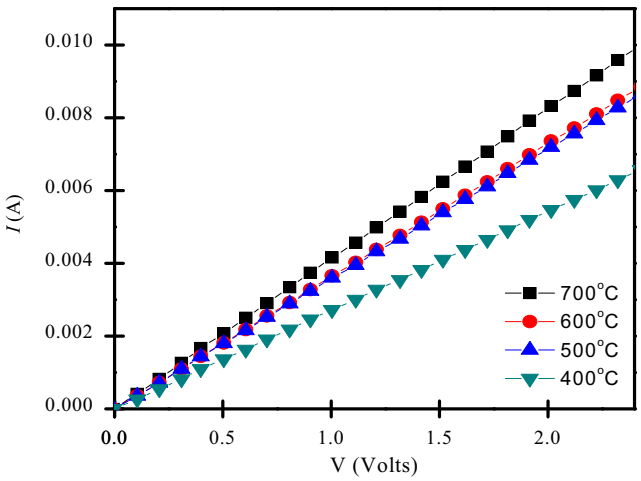

Fig. 6 *I-V* measurement of $Ni_{0.3}Zn_{0.7}Fe_2O$ nanoferrite thin films annealed at different temperatures

Magnetic properties

The hysteresis loop of Ni-Zn ferrite thin films as in Fig. 2. The magnetic parameters of saturation magnetization M_s and coercivity H_c are listed in Table 1. The M_s and H_c could be attributed to the varied grain size and crystallinity. The lower value of M_s. $Ni_{0.3}Zn_{0.7}Fe_2O_4$ films could be caused by the several reasons. Kumar et al. [21] stated that a large grain boundary volume presented in thin films would result in increase of the M_s. Other reasons the increase M_s are due to complex spinel structure, it was difficult to gain $Ni_{0.3}Zn_{0.7}Fe_2O$ nanoferrite films with perfect crystallization. The metal cations can occupy either *A* sites (tetrahedral) or *B* sites (octahedral), which will result in a partially disordered cation distribution in the crystal lattice [22]. The saturation magnetization (M_s) increases with the grain size, and the observations on larger decrease are interpreted mostly by oxygen absorption, characteristic to the preparation technique.

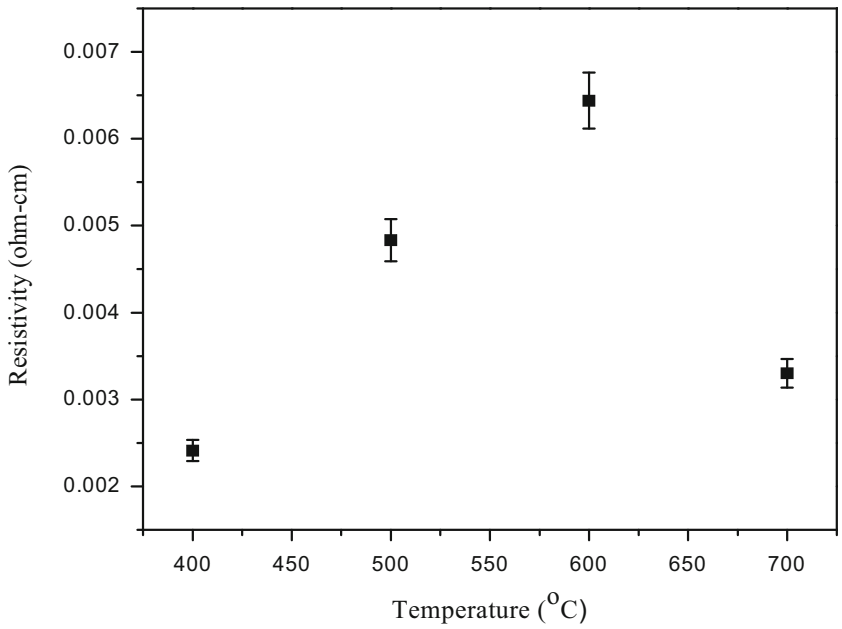

Fig. 7 Resistivity of samples at different annealing temperatures

The coercivity H_c was decreases as increase the annealing temperature and average grain size (Fig. 3). The maximum value of H_c was 16.54 Oe for the grain size 26.25 nm. The H_c observed were closed to Nie et al. [23] as reported that the value of H_c within the range 20–210 Oe. The decreases of H_c contributed from the transition of the single domain to the multidomain [24]. The coercivity (H_c) has a maximum at grain size of about 26 nm and a steep decrease at larger grain sizes (41.3 nm). The smaller grain sizes, the decrease of H_c due to the randomizing effects of thermal energy. Thermal energy is important role in magnetic instability of single domain magnetic particles. Due to the smaller grain sizes, the thermal agitation becomes small and will not be able to cause fluctuations in the magnetic spin orientations of the nanoparticles where they freeze in random orientations. The latter is probably due to the decreased anisotropy constant, which leads to a sharp decrease in coercivity according to the random anisotropy model. Relation of the decrease H_c as increase grain size as stated by Fernando et al. 2011 [25] that show the linear inverse proportionality between coercivity (H_c) and grain size (D) by $H_c \propto 1/D$.

Microstructure analysis

The FESEM images show the $Ni_{0.3}Zn_{0.7}Fe_2O_4$ films have dense and homogenous grains with an average grain size is tabulated in Table 2. The average grain size of the $Ni_{0.3}Zn_{0.7}Fe_2O_4$ nanoferrite thin films are 18.61 nm (400 °C), 26.25 nm (500 °C), 28.12 nm (600 °C) and 41.32 nm (700 °C). The grains of the films are spherical and uniform, and cohesion of grains is due to the magnetic attraction. The average grain size of the films is presented in Fig. 4. The histogram of grain size distribution shifted to the larger grain size as the annealing temperature increased. The grain size of the films also increases as temperature increases (Figs. 4 and 5).

Electrical properties

Figure 6 shows the linear curve of the *I-V* measurement of the $Ni_{0.3}Zn_{0.7}Fe_2O_4$ nanoferrite films in ambient light with voltage supply ranging from −10 to 10 V. Linear curves indicate that the gold metal contact show ohmic behaviour with the thin films. From the graph, it showed that the most conductive sample is 700 °C followed by 600, 500 °C and the least conductive is for sample sintered at 400 °C. From the *I-V* measurement, resistivity ρ were calculated and plotted as in Fig. 7. The resistivity ρ were found to increase with increase annealing temperatures, 2.4–6.4 × 10^{-3} Ωcm. The films perform a larger grain size with increase annealing temperature. The high resistivity 6.4 × 10^{-3} Ωcm can be due to the high band gap of the material and is within the range of the reported values [26]. The resistivity decreases at 700 °C due to the grain size increases (42.3 nm) as compared to 600 °C grain size of (28 nm). Increase annealing temperature leads to a decrease in grain boundaries and hence resistivity [26]. Smaller grains also imply smaller grain to grain surface contact area and therefore reduced the current flow, thus decrease the resistivity [27]. The conductivity σ graph plotted as a reciprocal of electrical resistivity. Conductivity σ of the $Ni_{0.3}Zn_{0.7}Fe_2O_4$ nanoferrite thin films showed a decreased in conductivity as the increasing annealing temperatures, 1.55–4.14 × 10^2 S-cm. The

conduction mechanism in ferrites is due to electron hopping of Fe^{2+} between Fe^{3+} ions and hole hopping between Ni^{2+} and Ni^{3+} at two adjacent B sites [28]. Zn is substituted with Ni in $Ni_xZn_{1-x}Fe_2O_4$, and enters the octahedral sites, whereas zinc has a strong affinity for tetrahedral sites. Therefore, a partial substitution of Ni for zinc dilutes the conduction mechanism occurring through octahedral sites [29].

Conclusion

Spherical $Ni_{0.3}Zn_{0.7}Fe_2O$ nanoferrite thin films with grain size of 18.6–42.3 nm have been fabricated via sol-gel synthesis and spin-coating method. XRD spectra confirm the films crystallinity increases with increase the annealing temperatures. Films annealed at 700 °C shows good crystallinity. EDX shows stoichiometric formation of $Ni_{0.3}Zn_{0.7}Fe_2O$ nanoferrite thin films. The Ni-Zn thin film was observed the presence of the superparamagnetic behaviour, as the smaller grain size range. Magnetic parameters M_s and H_c were observed as the M_s decreases and H_c increases with the increase annealing temperatures. The electrical resistivity of films was found to increase with increasing annealing temperature. This conventional process is a simple and very useful method to synthesize high-quality sphere-like Ni-Zn nanoferrite thin films. It will be promising low-cost alternative methods that produce high-quality thin films nanoferrite in the future.

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