



ISSN (Print) : 2320 – 3765

ISSN (Online): 2278 – 8875

International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering

(An ISO 3297: 2007 Certified Organization)

Vol. 6, Issue 7, July 2017

Co: Fe₂O₃, Co_xZn_{1-x}Fe₂O₄ Thin Films Grown by Chemical Spray Pyrolysis for Gas Sensor Application

Sevda S¹, Mutlu K¹, Omer C², Muhammet Y¹

¹Department of Physics, Ataturk University, 25250, Erzurum, Turkey

²Department of Electrical and Energy, Ispir Hamza Polat Vocational School of Higher Education, Ataturk University, 25250, Erzurum, Turkey

Abstract: Air pollution caused by toxic, flammable and explosive gases, detection of some hazardous gases is impossible for human, because some gases like CO and H₂ are odourless and tasteless as well as colourless. Furthermore in some cases absolute gas concentrations is very low to be detected by human nose. Therefore development and fabrication of a device for early detection of certain flammable, explosive, and toxic gases are extremely necessary. For this purpose, different devices have been developed toward tract detection of such pollution gases. Consequently, the development of cheap and reliable devices for detection of gases is considered to be a significant goal in science. In this study, iron oxide compound triple and quaternary iron oxide compounds with Zn, Co metal dopants were grown by using Chemical Spray Pyrolysis (CSP) technique. The structural, optical, magnetic properties of Co:Fe₂O₃, Co_xZn_{1-x}Fe₂O₄ compounds have been extensively investigated. XRD, Raman, SEM-EDAX and AFM techniques have been used for structural analysis; Absorption technique has been used for optical properties; Vibrating sample magnetometer (VSM) techniques have been used for magnetic properties. XRD analysis of the growth films revealed that Co:Fe₂O₃ film has monoclinic, Co_xZn_{1-x}Fe₂O₄ films have cubic polycrystalline structures. Gas sensors can be made from various materials depending on the purposes they serve. Regardless type of gas sensor, general requirements for a reliable gas sensor is high sensitivity, fast response, and good selectivity. It was found that Co:Fe₂O₃ and Co_xZn_{1-x}Fe₂O₄ thin films operating at 200°C temperature could detect H₂ at 100 ppm, 500 ppm and 1000 ppm concentration and at 600 s time with very high selectivity and sensitivity, with better stability.

Keywords: Gas sensor; Co:Fe₂O₃; Chemical spray pyrolysis (CSP); Thin film

I. INTRODUCTION

Interest in detecting and determining concentrations of toxic and flammable gases has constantly been on the increase in recent years due to increase of industrialization. Metal oxide gas sensors are among most important devices to detect a large variety of gases. α -Fe₂O₃, an environmental friendly semiconductor (e.g. = 2.1 eV), is the most stable iron oxide under ambient atmosphere and because of its low cost, high stability, high resistance to corrosion, and its environmentally friendly properties is one of the most important metal oxides for gas sensing applications [1].

In terms of gas sensor, α -Fe₂O₃-based sensors is widely applicable for the detection of various gases such as H₂, O₂, CO, H₂O etc. However, several obstacles have to be overcome for its future application. For example, the working temperatures are still high, and the recovery time is too long. These shortcomings can be partly avoided or improved by depositing noble metals, by composing with other semiconductors, and, most importantly, by introducing newly developed nanostructured α -Fe₂O₃ to the sensors. Pure α -Fe₂O₃ gas sensors are very cheap and are show higher sensitivity to ethanol and acetone, however they suffer from lack of selectivity and sometime low sensitivity.

The synthesis and functionalism of low dimensional nanostructured ferric oxide (α -Fe₂O₃) has fascinated the researchers due to their significant potential applications [2]. Various chemical pollutants have been released in high quantities into the atmosphere as a result of human activities and have generated environmental risks one of the critical factors that contribute to global warming, climate changes, and harm to human health. In order to monitor air pollution on a large scale, inexpensive, reliable and



International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering

(An ISO 3297: 2007 Certified Organization)

Vol. 6, Issue 7, July 2017

easy to use gas sensors are needed. The electrical resistance of semiconductor oxides, such as SnO_2 , ZnO , TeO_2 , WO_3 and Fe_2O_3 , has a strong dependence on the concentration of surrounding gases. According to this principle, these oxides are commercially designed as chemical sensors to detect toxic gases such as LPG, and NO_2 [3,4]. Ferric oxide is considered to be the most promising highly sensing materials of sensors due to the temperature dependent surface morphology and photo catalytic activity [5]. For gas sensing applications, the materials having lower density and higher active surface area are challenging for the fabrication of sensors.

II. EXPERIMENTAL DETAILS

The technique of CSP without the requirement of vacuum is a method that can be preferred in the industry, in order to allow the production of large size films in both cheap. However, there are some disadvantages of films made with this technique, such as their thickness being not uniform and the size of the film-forming atoms being limited and the film in chemical solution to be grown must be homogeneous. Many parameters such as substrate, substrate temperature, the salts, solvent type, molarity and deposition time have carefully been chosen to obtain the best growth condition in this technique. The salts given in Table 1 were prepared as 0.1 molar solution in deionized water. The substrate was sprayed with argon gas onto a substrate heated to 320°C at a distance of 30 cm.

Film	Used Chemical Salt	Solution Molar Ratio	Substrate Temperature ($^\circ\text{C}$)	Carrier gas	Grown Time (min)
$\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{FeCl}_2 \cdot 4\text{H}_2\text{O} + \text{NaOH} + \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1:2:0.25:0.1:0.01	320	Argon	35
$\text{Co}:\text{Fe}_2\text{O}_3$	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{FeCl}_2 \cdot 4\text{H}_2\text{O} + \text{NaOH} + \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1:2:0.25:0.1	320	Argon	35

Table 1: Experimental details of the $\text{Co}:\text{Fe}_2\text{O}_3$ and $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ thin films grown by chemical spray pyrolysis technique.

III. RESULTS AND DISCUSSION

The structural, optical and magnetic properties of $\text{Co}:\text{Fe}_2\text{O}_3$ and $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ compounds have been extensively investigated. XRD, Raman, SEM-EDAX and AFM techniques have been used for structural analysis; Absorption technique has been used for optical properties; Vibrating sample magnetometer (VSM) techniques have been used for magnetic properties and I-V technique has been used for response of gas sensor Figure 1 and Table 2 [6].



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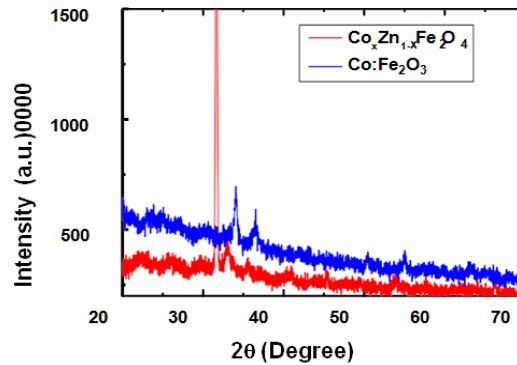


Figure 1: XRD patterns of Co:Fe₂O₃ and Co_xZn_{1-x}Fe₂O₄ thin films.

Literature 2θ°	Experimental 2θ°	(hkl)	Fwhm	Lattice constant	d (Å)	Crystal system	Chemical formula	Reference Code
34,84	34,11	-213	0.34	a=12,97 b=10,21 c= 8,44	2,57	Monoclinic	Fe ₂ O ₃	00-016-0653
36,52	36,81	23	0.17	a=12,97 b=10,21 c= 8,44	2,45	Monoclinic	Fe ₂ O ₃	00-016-0653
50,46	50,43	-631	0.11	a=12,97 b=10,21 c= 8,44	1,80	Monoclinic	Fe ₂ O ₃	00-016-0653
55,08	55,10	352	0.09	a=12,97 b=10,21 c= 8,44	1,66	Monoclinic	Fe ₂ O ₃	00-016-0653

Table 2: Structural properties obtained from XRD patterns of Co:Fe₂O₃ thin film.

Experimental 2θ°	(hkl)	Fwhm	d (Å)	Crystal system	Chemical formula	Lattice constant	Reference Code
31,71	220	0,155	2,81	Cubic	ZnCo ₂ O ₄	a= b=c=8.42	00-001-1149
32,97	222	0,035	2,71	Rhombohedral	Fe ₂ O ₃	a=b=5,03 c=13,74	01-079-1741
35,45	311	0,11	2,53	Cubic	(Zn _{0.54} Fe _{0.46}) Fe ₂ O ₄	a=b=c=8,42	01-086-0509
66,29	442	0,090	1,41	Cubic	(Zn _{0.54} Fe _{0.46}) Fe ₂ O ₄	a=b=c= 8,42	01-086-0509

Table 3: Structural properties obtained from XRD patterns of Co_xZn_{1-x}Fe₂O₄ thin film.

International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering

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Vol. 6, Issue 7, July 2017

XRD analysis of the growth films revealed that Co:Fe₂O₃ film has monoclinic and Co_xZn_{1-x}Fe₂O₄ films have heavily cubic polycrystalline structures. XRD results indicated that cobalt successfully replaced iron in the host lattice. The peak positions shifted to higher angles due to lower ionic radius of cobalt as compared to that of iron Table 3.

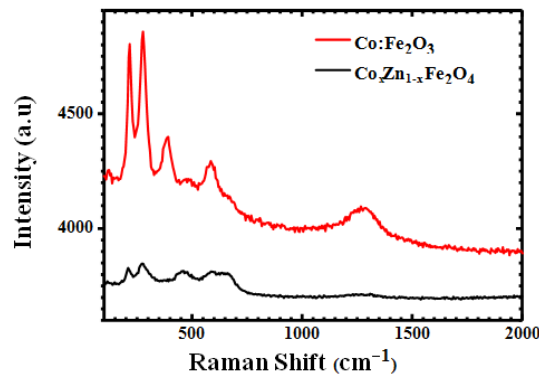


Figure 2: Raman scattering intensities are shown as a function of wavenumber for Co:Fe₂O₃ ve Co_xZn_{1-x}Fe₂O₄ thin films.

Figure shows the Raman shift of the stretching vibration mode of Co:Fe₂O₃ films are seen. There are Raman active states of the hematite phase that these peaks are relatively narrow and severe. In the Co_xZn_{1-x}Fe₂O₄ compound, the peak of the Raman shift peaks belonging to the hematite phase falls (Figure 2). In addition, the peaks showing the ramping changes of the stretching vibration mode of the Co_xZn_{1-x}Fe₂O₄ film is due to the presence of multiple phases due to polycrystalline crystal structure and also impurity, oxygen vacancies, interstitial ion [7-11] (Table 4).

Compounds	Raman Shift (cm ⁻¹)	Mod
Fe ₂ O ₃	217;277; 388;584; 1284; 2891;	Hematit; [(A1g) 225], [(A1g) 229], [(Eg) 247], [(Eg) 249], [(Eg) 295],[(Eg) 302], [(Eg) 412], [(A1g) 500], [(Eg) 615],[(Eu) 660 LO] , [(a-Fe ₂ O ₃) 1320] [12-14]
Co _x Zn _{1-x} Fe ₂ O ₄	117; 145; 206; 273; 464; 591; 656; 1286	Hematit [(A1g) 229], [(Eg) 247],[(A1g) 225] [A1g (Co _x Zn _{1-x} Fe ₂ O ₄) (464-656)] , [(a-Fe ₂ O ₃) 1320] [15]

Table 4: Raman shift and modes of Co: Fe₂O₃ and Co_xZn_{1-x}Fe₂O₄ thin films.

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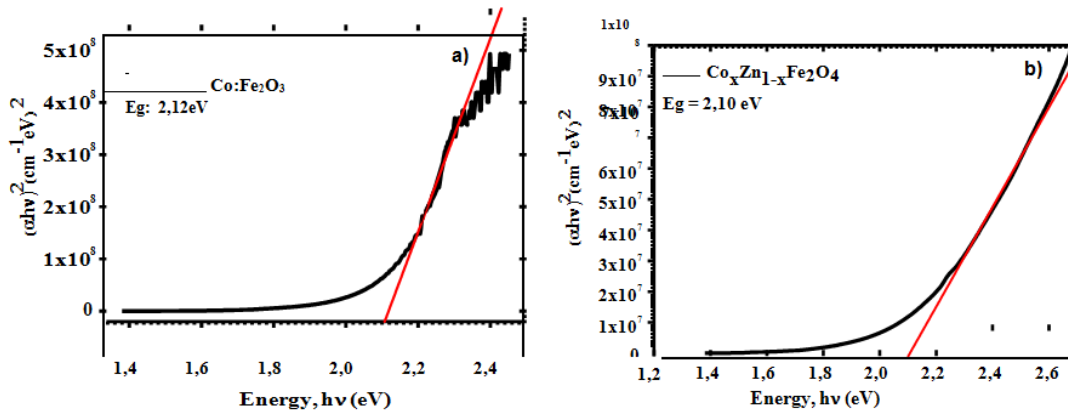


Figure3: Plot of $(\alpha hv)^2$ vs. photon energy $h\nu$ of a) Co: Fe_2O_3 b) $Co_xZn_{1-x}Fe_2O_4$ thin films.

In Figure 3 the value of the energy of the band gap is calculated to be 2.10 eV, 2.12 eV with the fit drawn on the energy graph against the $(\alpha hv)^2$ ($cm^{-1} eV^2$) of the Co: Fe_2O_3 , $Co_xZn_{1-x}Fe_2O_4$ thin films grown by CSP technique, respectively. As $Co_xZn_{1-x}Fe_2O_4$ thin film gives absorption at smaller wave lengths, it shifts at larger wave length as a result of doping. We can say that the holes in the valence band of the p-type semiconducting material are compensated by the donor type defects and impurities. This may mean that the energy gap of $Co_xZn_{1-x}Fe_2O_4$ is larger than Co: Fe_2O_3 band gap.

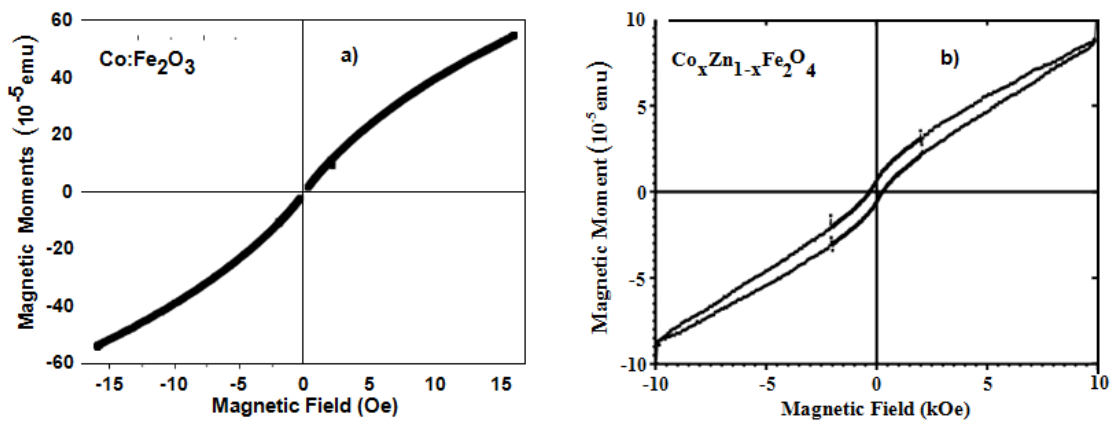


Figure 4: M-H curves for a) Co: Fe_2O_3 and b) $Co_xZn_{1-x}Fe_2O_4$ thin films.

In Figure 4a the magnetic hysteresis curve of the Co: Fe_2O_3 thin film is observed to be relatively narrow. The saturation magnetic torque value is $55.5 \cdot 10^{-5}$ emu, which corresponds to a value of 15.94 Oe. In addition, the coercive force is -0.008 Oe and the remanence magnetic moment is 0.063. It has an emu value of 10^{-5} . In these values, it has been determined that Co: Fe_2O_3 has a soft magnetic property.

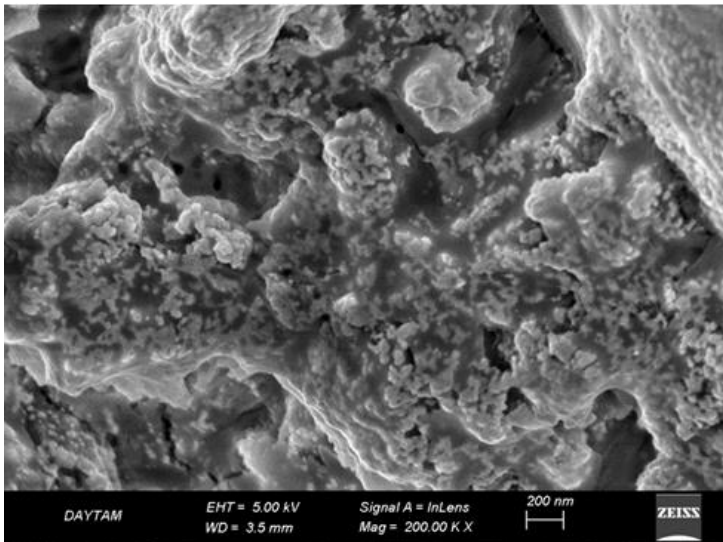
Among the various phases of iron oxide, Fe_2O_3 is the most stable form of iron oxide that shows antiferromagnetic behaviour. Doping of different metal ions in a- Fe_2O_3 will lead to its new technological and industrial applications and enhancement of its performance in existing applications. Cobalt doped Fe_2O_3 thin films showed ferromagnetic behavior because of the presence of uncompensated spins arising from cobalt doping [11-15].

International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering

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Vol. 6, Issue 7, July 2017

In Figure 4 the magnetic hysteresis curve of the Co: Fe₂O₃ thin film is observed to be relatively narrow. The saturation magnetic torque value is $55.5 \cdot 10^{-5}$ emu, which corresponds to a value of 15.94 Oe. In addition, the coercive force is -0.008 Oe and the remanence magnetic moment is 0.063. It has an emu value of 10^{-5} . When the hysteresis curve is taken into consideration, it can be said that the material exhibits hard magnetism and is difficult to demagnetize due to the Zn doping. The nonmagnetic property of the Zn element affects the magnetic moment of the Zn doping which leads to pinning spin and makes the domain motion difficult.



Element	Mass %	Atomic%
Fe	35.84	18.72
O	40.1	64.68
Zn	5.33	1.91
Cl	5.27	0.37
Au	3.02	0.47
Co	4.44	2.32

Figure 5: FE-SEM images and EDX analysis table of Co_xZn_{1-x} Fe₂O₄ thin film.

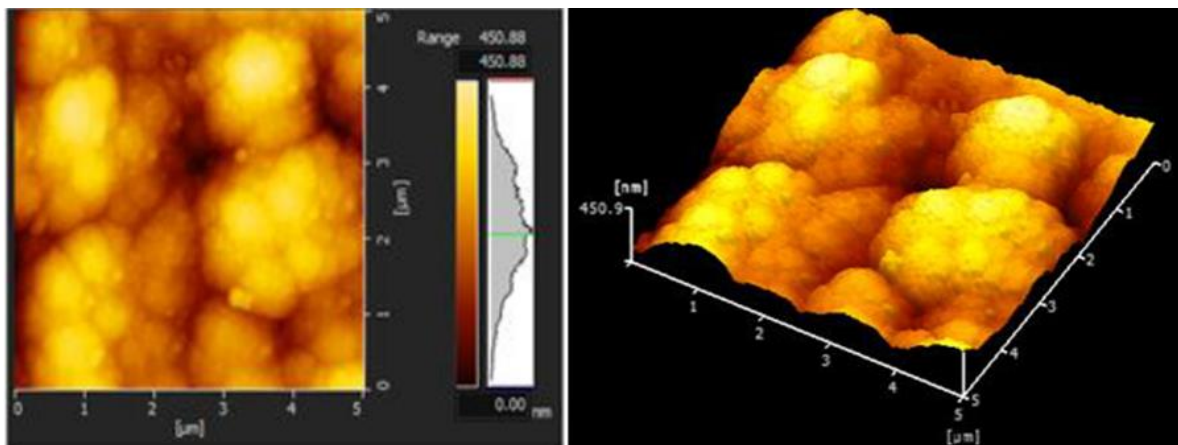


Figure 6: Two-dimensional and three-dimensional AFM images of the Co_xZn_{1-x} Fe₂O₃ thin film grown on glass substrates. The Co_xZn_{1-x} Fe₂O₃ films line roughness value is about 49 nm.

International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering

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Vol. 6, Issue 7, July 2017

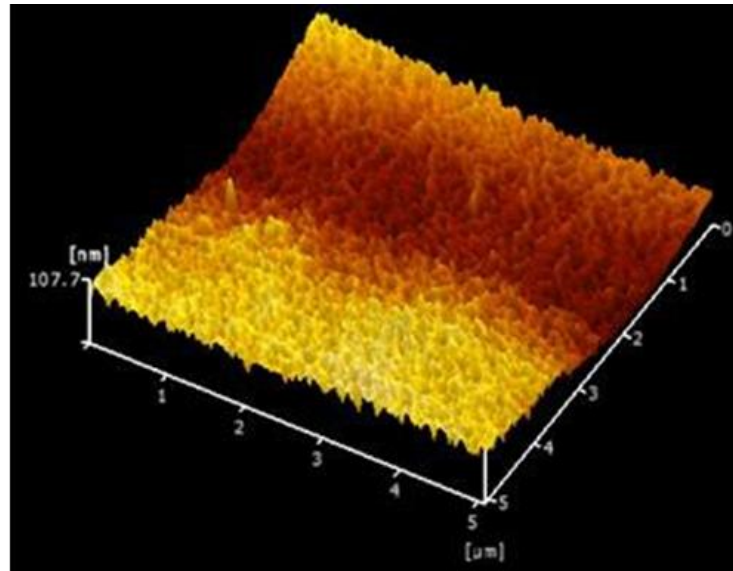
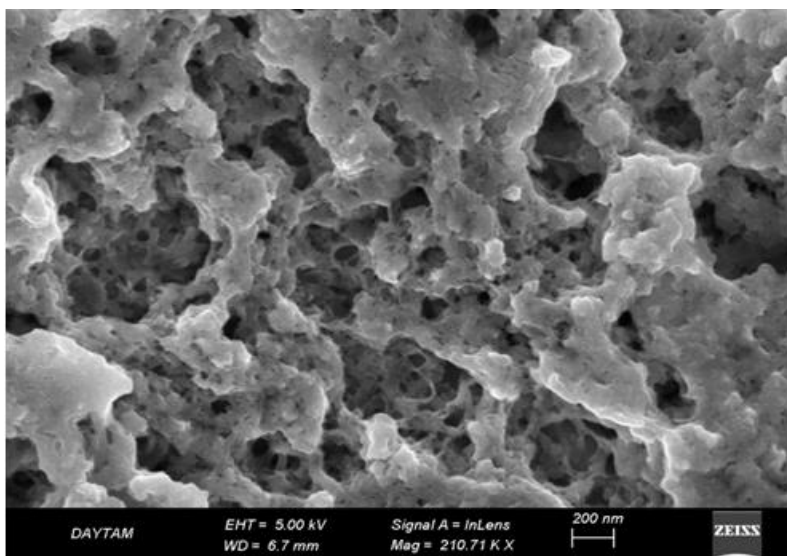


Figure 7: AFM images of the $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ thin film grown on glass substrates (5 minutes grown). The $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ films line roughness value is about 6.9 nm.

The nano-pores found in the FE-SEM image of the $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ (5 minutes grown) structure show a sharp-pointed sequence with a clearly noticeable structure. The thickened residues formed concentrated areas due to gravity. When the structure is thin, the interactions vary in thickness. The structure is arranged very regularly and is clearly observed. Thickness of the grain at the surface of the crystal is much larger than that of the crystal. The $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ films roughness value is about 49 nm (Figures 5 to 7).



Element	Mass %	Atomic%
Fe	47.64	26.87
O	33.96	56.01
Cl	14.53	12.91
Co	7.87	4.2

Figure 8: FE-SEM images and EDX analysis table of $\text{Co: Fe}_2\text{O}_3$ thin film.

International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering

(An ISO 3297: 2007 Certified Organization)

Vol. 6, Issue 7, July 2017

The Co: Fe₂O₃ compound appears to have a nanoporous structure in the SEM image taken from an area of 200 nm at 210,000 magnifications taken from the inlens detector. This literature study suggests that it is suitable for supercapacitor and gas sensor application [7-10]. Cl element in the EDX results are due to salts used in the solution and the Au element in the EDX results is due to the coating made to clarify the image during FE-SEM measurement. We can say the Cl element remained unvaporized due to the low substrate temperature (Figure 8).

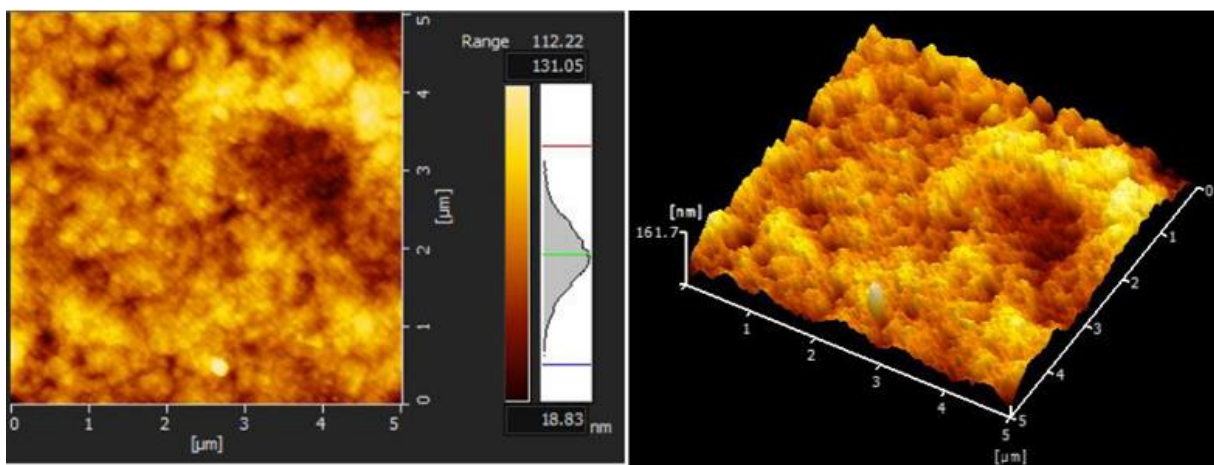
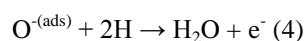
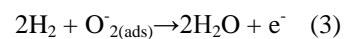
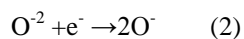
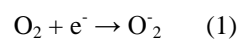


Figure 9: Two-dimensional and three-dimensional AFM images of the Co: Fe₂O₃ thin film grown on glass substrates. The Co: Fe₂O₃ films line roughness value is about 10 nm.

In Figure 9 the two-dimensional and three-dimensional AFM images obtained for the Co: Fe₂O₃ film showed that the particles in the structure showed a more sharp image. There are pits and hills almost everywhere in the landscape resembling craters. The roughness value is about 10 nm. The variability of the colors tone indicates that the height difference in the topography is great. It is possible to say that the surface consists mostly of hills and pits.

When we get the gas sensor measure we see that Co: Fe₂O₃ and Co_xZn_{1-x}Fe₂O₄ is the n type semiconductor. Because of the electrons that emerge as a result of the reaction increase the carrier concentration. Thus resistance is reduced.



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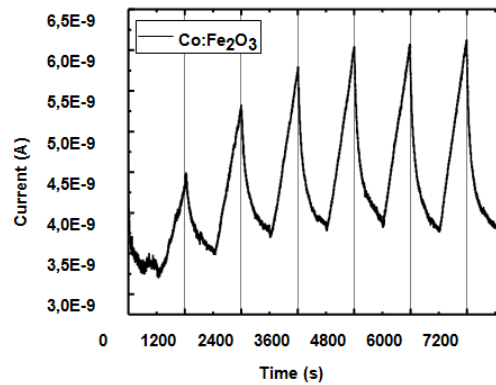


Figure 10: Sensor Response of Co: Fe₂O₃ thin film deposited by using Chemical Spray Pyrolysis (CSP) technique towards H₂ target gases for different concentrations (100 ppm, 500 ppm, 1000 ppm) at 200°C temperature.

In Figure 10 Co: Fe₂O₃ shows the time-dependent change in the response of the thin film to hydrogen gas, and the measurement is periodically 600 s nitrogen and 600 s hydrogen gas at 200°C. This measurement was made to evaluate the response of the thin film to hydrogen gas, and the reaction of the film to hydrogen gas was found to be very high. During the measurement periodically 600 s nitrogen and 600 s hydrogen gas were supplied to the system at 200°C temperature. The film, which did not react to hydrogen gas at room temperature, reacted at a temperature of 200°C. Nitrogen was used as the sweeping gas. In the first 600 s 500 ppm nitrogen swept system, 100 ppm hydrogen gas was then supplied and the amount of current drawn by the system increased. When the nitrogen is swept in again, the current drawn is reduced and receded to the previous level. 500 ppm for 600 s in the second cycle, 1000 ppm for 600 s in the third cycle and the current value increased with the hydrogen value. The same gauge is repeated after 24 hours and the same result was obtained. This material is a promising material for gas sensor application.

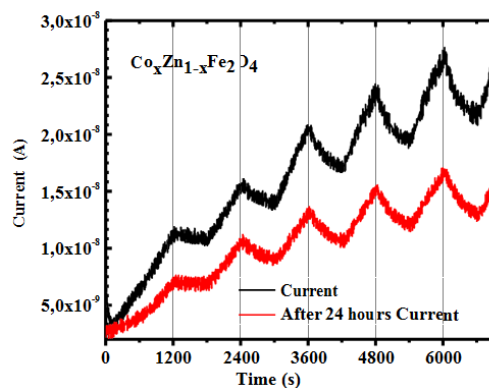


Figure 11: Sensor Response of Co_xZn_{1-x}Fe₂O₄ thin film deposited by using CSP technique towards H₂ target gases for different concentrations (100 ppm, 500 ppm, 1000 ppm) at 200°C temperature.



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As mentioned earlier, there is a gas sensor application of the $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ compound in the literature. In addition to being used for spintronic applications due to its magnetic properties, it is available in gas sensor applications due to the large surface area of the material with a thickness of 100 nm and above [6]. In Figure 11, $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ shows the time-dependent change in the response of the thin film to hydrogen gas, and the measurement is periodically 600 s nitrogen and 600 s hydrogen gas at 200°C. This measurement was made to evaluate the response of the thin film to hydrogen gas, and the reaction of the film to hydrogen gas was found to be very high. During the measurement periodically 600 s nitrogen and 600 s hydrogen gas were supplied to the system at 200°C temperature. The film, which did not react to hydrogen gas at room temperature, reacted at a temperature of 200°C. Nitrogen was used as the sweeping gas. In the first 600 s 500 ppm nitrogen swept system, 100 ppm hydrogen gas was then supplied and the amount of current drawn by the system increased. When the nitrogen is swept in again, the current drawn is reduced, but not receded to the previous level. This means that some of the hydrogen remains in the structure. 500 ppm for 600 s in the second cycle, 1000 ppm for 600 s in the third cycle and the current value increased with the hydrogen value. The same gauge is repeated after 24 hours, indicating that hydrogen is held at a lower level, which means that the hydrogen is stored in the structure, during which the hydrogen is separated from the structure in very small amounts. This material is a promising material for gas sensor application as well as promising hydrogen storage applications 100; R sensors response, I ; first current, I finally current. According to calculations made, Table 5 gives the respons of the gas sensors.

Time	600.s	1200.s	1800.s
Compound	(100 ppm)	(500 ppm)	(1000 ppm)
Co: Fe_2O_3	23.33%	35%	38%
$\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$	11%	18.35%	22%
$\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ After 24 hour	10.59%	22%	27%

Table 5: $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ and Co: Fe_2O_3 gas sensors respons depends of gas flow rate.

III. CONCLUSION

This material is a promising material for gas sensor application as well as promising hydrogen storage applications. When we consider the magnetization situation, the hardest magnetization property is $\text{Co}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ film, the softest magnetization feature is Co: Fe_2O_3 film. It can be said here that Zn, which has no magnetic property, causes pinning which make defects in the structure difficult to move the domains. As can be seen from the VSM results, these materials can also be used for spintronic applications.

IV. REFERENCE

1. Mirzaei A, Hashemi B, et al. A- Fe_2O_3 based nanomaterials as gas sensors. J Mater Sci: Mater Electron 2016; 27: 3109–3144.
2. Mukherjee S, Pal AK, EPR Studies on sol–gel derived Fe_2O_3 nanocrystals in SiO_2 matrix, Proceedings of the First International



ISSN (Print) : 2320 – 3765

ISSN (Online): 2278 – 8875

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(An ISO 3297: 2007 Certified Organization)

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Symposium. Solid State Physics 2003; 23: 205–206.

3. Sonker RK, Yadav BC, Chemical Route Deposited SnO₂, SnO₂-Pt and SnO₂-Pd Thin Films for LPG Detection. Adv. Sci. Lett., 2014; 20: 1023-1027.

4. Sonker RK, Yadav BC, Synthesis of ZnO nanopetals and its application as NO₂ gas sensor. Materials Letters 2015; 152: 189–191.

5. Chaudhari NK, Yu JS, Size control synthesis of uniform β -FeOOH to high coercive field porous magnetic α -Fe₂O₃ nanorods. J. Phys. Chemistry C 2008; 112: 19957–19962.

6. Panda J, Nath TK, Low temperature junction magnetoresistance properties of Co_{0.65}Zn_{0.35}Fe₂O₄/SiO₂/p-Si magnetic diode like heterostructure for spin-electronics. Thin Solid Films 2016; 601; 111–118.

7. Ho MY, Khiew PS, Shamsuddin, Nano Fe₃O₄-activated carbon composites for aqueous supercapacitors. Sains Malaysiana 2014; 43: 885–894.

8. Lokhande CD, Dubal DB, Metal oxide thin film based supercapacitors. Curr Appl Phys 2011; 11: 255–270.

9. Ilgeun O, Kim M, Controlling hydrazine reduction to deposit iron oxides on oxidized activated carbon for supercapacitor application. Energy 2015; 86: 292–299.

10. Pawar NK, Kajale GH, Nanostructured Fe₂O₃ thick film as an ethanol sensor. International Journal on Smart Sensing and Intelligent Systems 2012; 5: 2.

11. Aseya A, Sidra B, Magnetic Properties of Co-doped Fe₂O₃ Thin Films. Materials Today: Proceedins 2015; 2: 5674 – 5678.

12. Chamritski I, Burns G, Infrared-and Raman-active phonons of magnetite, maghemite, and hematite: a computer simulation and spectroscopic study. J Phys Chem B 2005; 109: 4965–4968.

13. Bersani D, Lottici P, Micro-Raman investigation of iron oxide films and powders produced by sol–gel syntheses. J Raman Spectrosc 1999; 30: 355–360.

14. Jubb AM, Allen HC, Vibrational spectroscopic characterization of hematite, maghemite, and magnetite thin films produced by vapor deposition. Applied materials and interface 2010; 2: 2804–2812.

15. Rahimi M, Kameli P, The effect of zinc doping on the structural and magnetic properties of Ni_xZn_{1-x}Fe₂O₄. J Mater Sci 2013; 48: 2969–2976.