CHAPTER - 2

PREPARATION AND CHARACTERIZATION OF THIN FILM SENSORS

2.1 Introduction

This chapter deals with fabrication of samples as undoped zinc oxide flat thin film, 8 % Fe doped nano-wrinkled, 8 % Cu, Co, Ni doped zinc oxide thin films, undoped ZnO nano-wired, 8 % Cu doped ZnO nano-strips and 8 % Fe doped ZnO nano-net thin films using technique of spin coating and drop casting on glass substrates.

2.2 Undoped Zinc Oxide Flat Thin Film

The deposition of thin film of undoped Zinc oxide is carried out by spin coating method. 0.65847g Zinc acetate $(CH_3COO)_2Zn{\cdot}2H_2O$ [99.99 % Pure Powder, Sarabhai M. Chemicals] was dissolved in the 10 ml 2-methoxyeathnol ($C_3H_8O_2$) [Merck Specialties (P)] for 0.3 M solution, it was kept under continuous magnetic stirring at the 35 $^{\circ}$C for one half hour (1/2 h). Further, diethyl amine ($C_4H_{11}N$) was added under continuous stirring condition till colorless homogeneous solution was achieved. Substrate prepared was used for deposition process and kept on spin coater, hold by vacuum and spin at 500 rpm initially and one drop was casted at the spinning substrate, further rpm was increased to 1500 rpm, then to 2000 rpm, 2500 rpm and 3000 rpm and holding time for each steps of rotation is 1 min and at every step one drop was casted. After spin coating, sample was kept on hot plate at 250 °C for 2 min for drying. Further spinning and drying was repeated 5 times and there after sample was kept in the preheated furnace for 30 minutes at 300 °C and continuously it was heated further at 450 °C for 30 minutes. A thickness of the deposited Zinc Oxide thin film was 1.45 µm. The

metallization is done using paste deposited method. Fabricated sensor sample is shown in Fig 2.1.

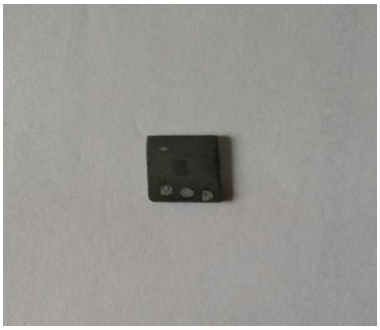

Fig.2.1. Photograph of fabricated undoped ZnO thin film sensor.

The X-ray diffraction characterization confirms the nano-crystalline hexagonal structure of zinc oxide thin film deposited on the glass substrate. Peaks are identified to zinc oxide diffraction pattern (JCPDS No- 36-1451) with absence of impurities (Fig.2.2).

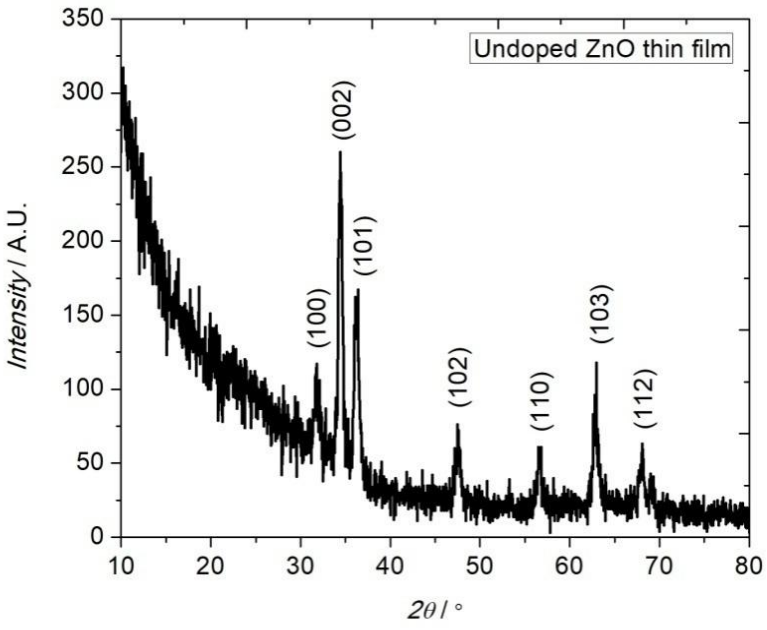

Fig.2.2. XRD pattern of undoped ZnO thin film.

SEM characterization (Fig.2.3 and Fig.2.4) confirm the thin film structure, one dimensional, uniform and smooth, dense, porous, nano and micro-wires equivalent structure with flat surface on glass substrate was demonstrated and also, it confirm that specific nano structures such as wrinkle, nano strips etc., are not developed. The SEM characterization indicated that the film is suitable for gas sensing.

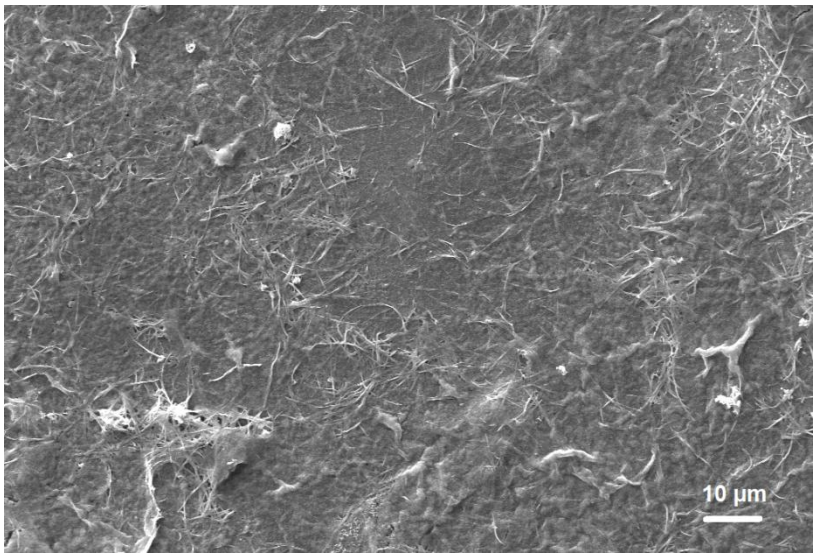

Fig.2.3. SEM of undoped ZnO thin film (2.00 K X Magnification)

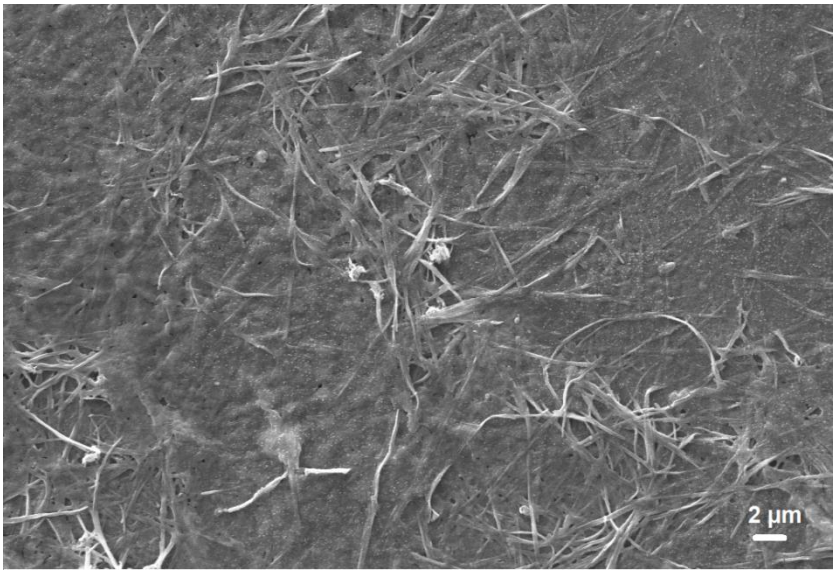

Fig.2.4. SEM of undoped ZnO thin film (5.00 K X Magnification)

EDX images (Fig.2.5) show that the zinc peaks in the range of 10 MeV electron binding energy and confirms the compositions as undoped zinc oxide.

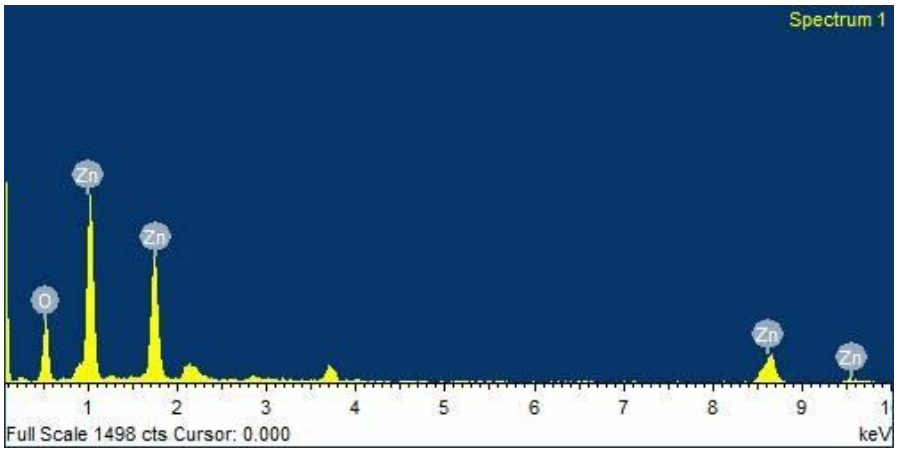

Fig.2.5. EDX of undoped ZnO thin film.

The Roughness of the film was in the range of 40 to 80 nm (average 75.7 nm) as determined by AFM (Fig. 2.6 and Fig. 2.7). These 2D and 3D-AFM images confirm the flat structure of zinc oxide film because there is not other nano structure shown in film. So, film was suitable for gas sensing due to roughness is below 100 nm.

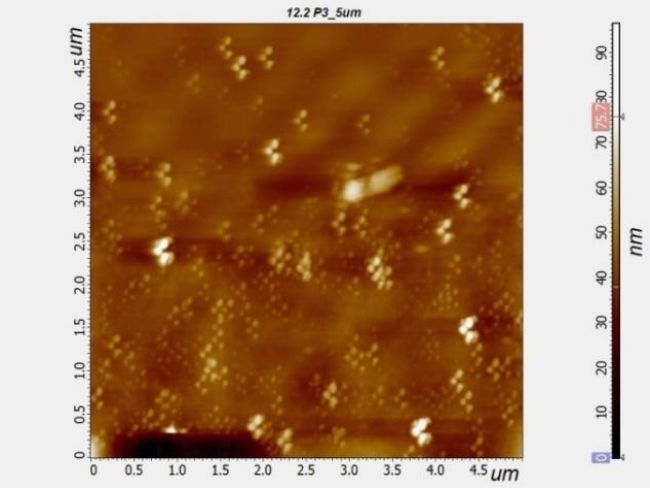

Fig.2.6. 2D-AFM of undoped ZnO thin film

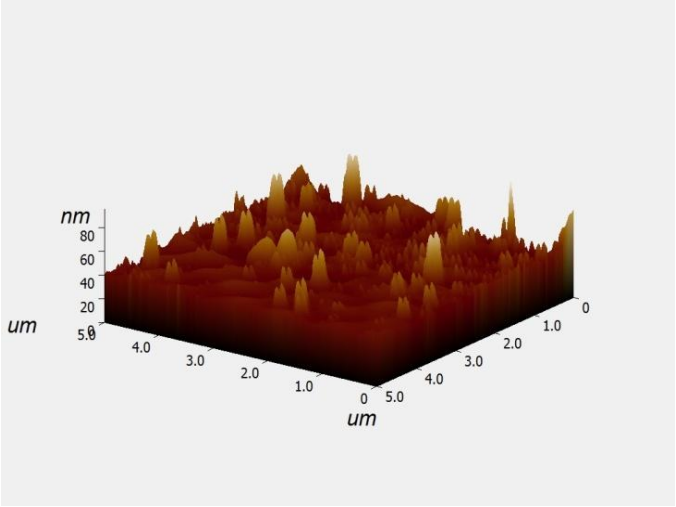

Fig.2.7. 3D-AFM of undoped ZnO thin film.

2.3 Fe Doped Zinc Oxide ($Zn_{0.92}Fe_{0.08}O$) Nano-Wrinkled Thin Film

0.65847g Zinc acetate [$(CH_3COO)_2Zn{\cdot}2H_2O$] [99.99 % Pure Powder, Sarabhai M. Chemicals] was dissolved in the 10 ml 2-methoxyeathnol ($C_3H_8O_2$) to make 0.3 M solution and it was kept under continuous magnetic stirring at the 35 $^{\circ}$C for half hour. Further, diethyl amine ($C_4H_{11}N$) [Merck Specialties (P) Ltd.] was added in to it under continuous stirring till homogeneous solution was achieved. 1.212 g Ferric Nitrate [Fe $(NO_3)_3{\cdot}9H_2O$] [99.99 % Pure powder, Qualigense fine chemicals] solution was also made by same method without using diethyl amine. Further ferric nitrate solution into zinc acetate solution in the ratio of doping and stirrer till transparent as golden brown solution at 35 $^{\circ}$C. Substrate prepared was used for deposition process and kept on spin plate, hold by vacuum and spin at 500 rpm initially and one drop was casted at spinning substrate, further rpm was increased to 1500 rpm, then to 2000 rpm, 2500 rpm and 3000 rpm and holding time for each steps of rotation is 1 min and at every step one drop was casted. After spin coating, sample was kept on hot plate 250 °C for 2 min for drying. Further spinning and drying was repeated 5 times and there after sample was kept in furnace for 30 minutes at 300 °C and continuously it was heated further at 450 °C for 30 minutes. In this way, we deposited the zinc oxide and Fe doped ZnO films on the glass substrate by the electro-spin rpm pattern from 500 to 3000 rpm. Silver contacts were made by the paste method using dotted aluminum metal mask and keep in oven at 250 °C for one half hour for drying. Thickness the film was found close to 1.40 μm. Fig.2.8 shown the photograph of fabricated Fe doped ZnO or $Zn_{0.92}Fe_{0.08}O$ thin film sensor.

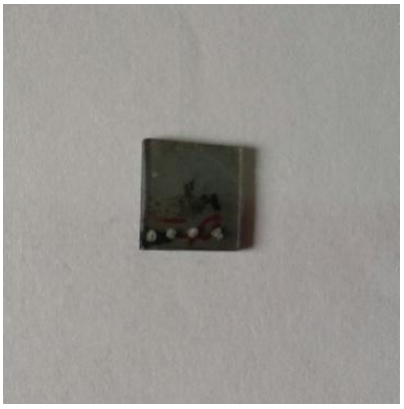

Fig.2.8. Photograph of fabricated $Zn_{0.92}Fe_{0.08}O$ thin film sensor.

Fig.2.9 shows the XRD pattern of the deposited film. Diffraction peaks confirm that the film is polycrystalline and have hexagonal wurtzite crystal structure (JCPDS No. 36-1451), as deposited on the glass substrate. Peaks are indicated to zinc oxide with absence of impurities and, also peaks intensity decreased compared to undoped ZnO thin film due to 8 % Fe doping into host lattice without any change of structure.

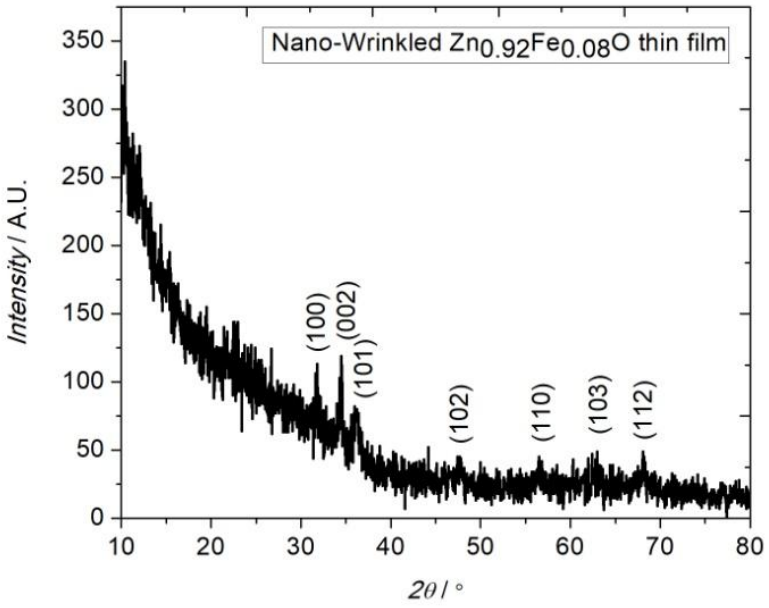

Fig.2.9. XRD pattern of $Zn_{0.92}Fe_{0.08}O$ thin film.

In the Fig.2.10 and Fig.2.11, SEM images are shown, SEM study confirm the smooth and uniform wrinkled film formation on glass substrate. The wrinkles grown on the film are of the various thicknesses such as 62 nm, 315.15 nm, 715.2 nm etc. The gas molecules can interact with the film then adsorb on to nano-wrinkles as well as smooth surface and undergo though the reduction process. The designed wrinkles can act as active centre for gas adsorption. Wrinkles can increased the chemisorptions sites at the surfaces and provide the large surfaces for adsorptions. The film grown better than undoped zinc oxide based thin film.

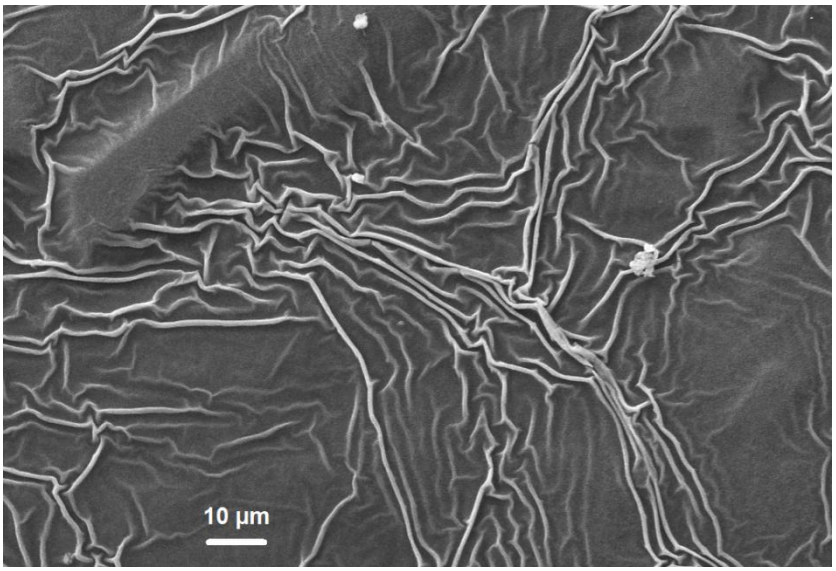

Fig.2.10. SEM of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film (2.00 K X Magnification)

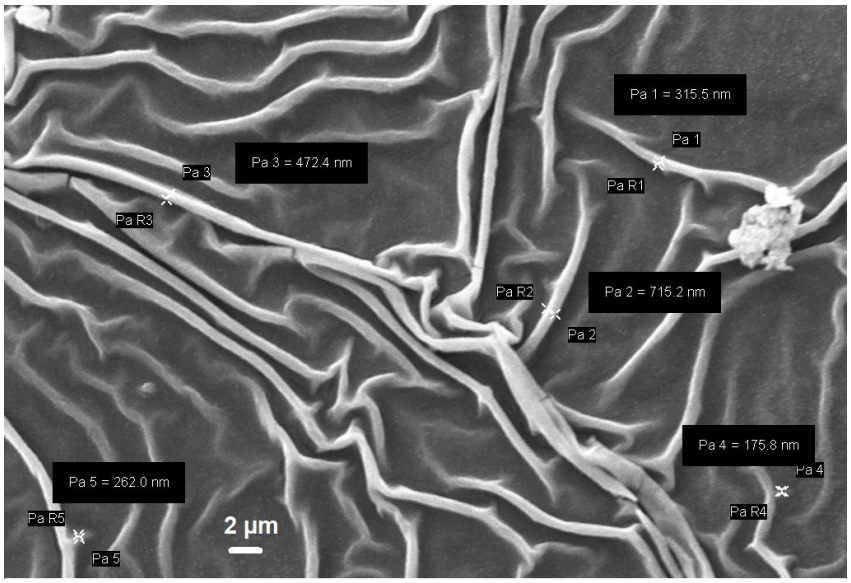

Fig.2.11. SEM of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film (5.00 K X Magnification)

Field Emission Scanning Electron Microscopy (FE-SEM) / HR-SEM, studies also clearly reveal the increased in active surface of the film at the place of developed wrinkled structure (Fig.2.12, Fig.2.13, Fig.2.14 and Fig.2.15). The thicknesses of the winkles were in the ranges of 153 nm, to 222 nm etc and particles are of the sizes 36 nm, to 47 nm (Fig.2.14 and Fig.2.15). Particles or crystallites at wrinkles are of sizes 26 to 52 nm. However, the particles are of sizes 28 to 42 nm at flat part of the wrinkled structured film (Fig.2.13, Fig.2.14 and Fig.2.15). The analysis of surface of wrinkle also confirms the formation of a dense nano-crystallites and smooth surface on wrinkle. This results into increase in surface area from surface to surface. Therefore, as surface area increases, the adsorption sites increases, hence adsorption must be increased at wrinkles structure resulting into enhanced sensing activity of the film.

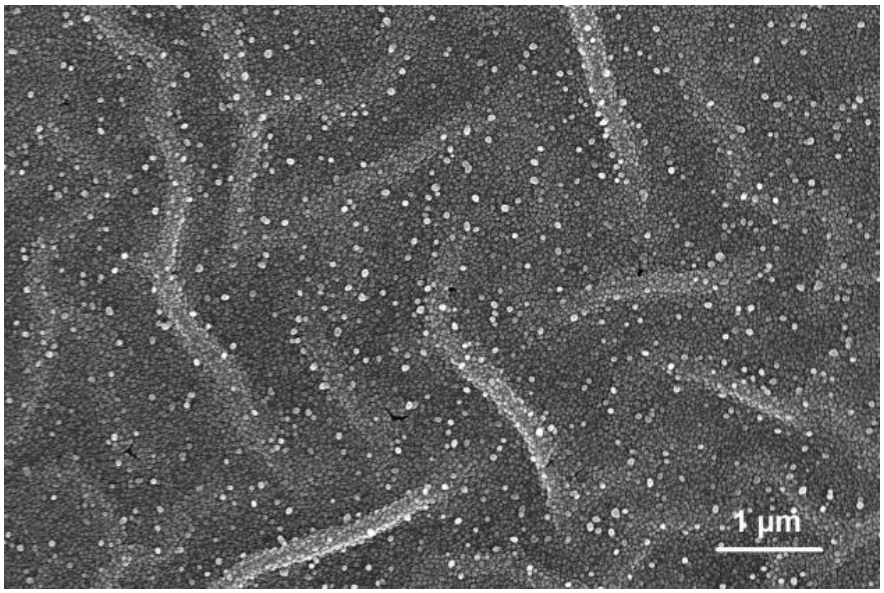

Fig.2.12. FE-SEM of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film showing; large area view.

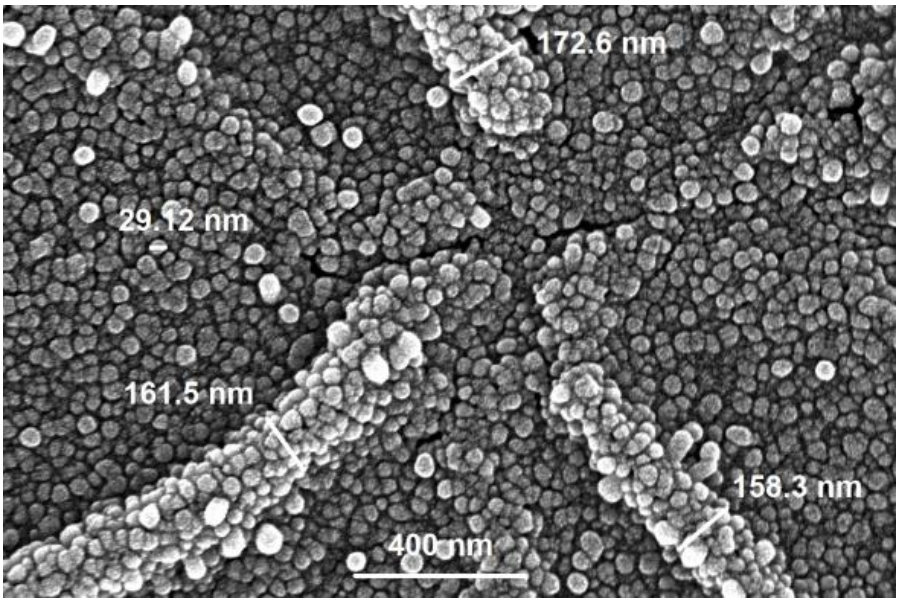

Fig.2.13. FE-SEM of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film showing; enlarged structure.

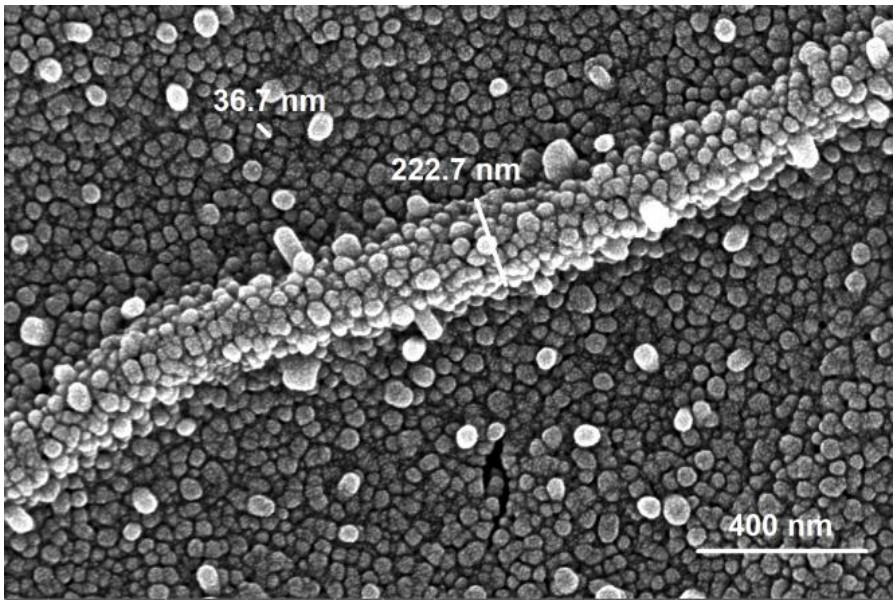

Fig.2.14. FE-SEM of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film showing; grown single wrinkle.

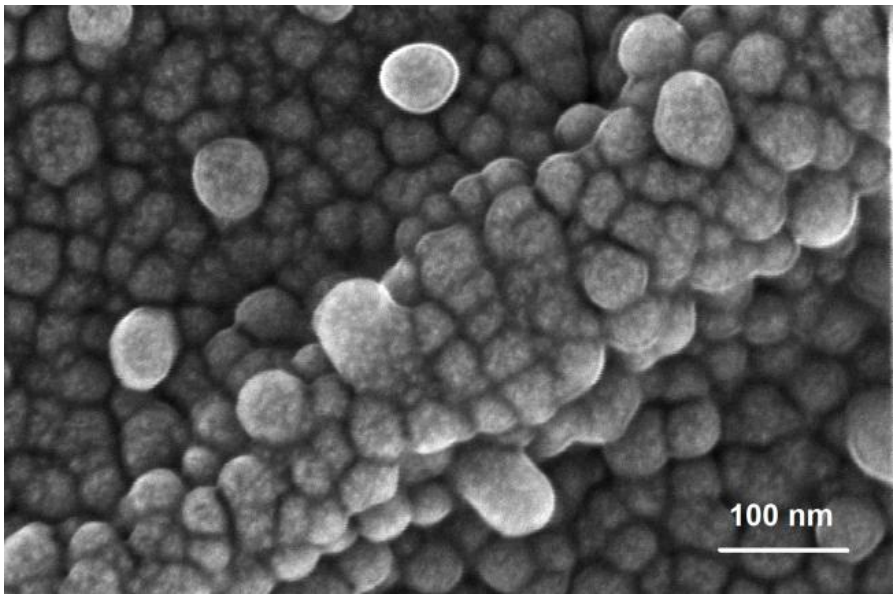

Fig.2.15. FE-SEM of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film showing; wrinkle surface and grain /grain boundary structure.

Fig.2.16 showed the EDX (Energy dispersive X-ray) image that verifies the compositions of the grown film. The composition of the film (Fe/Zn) is found almost same to the nominal composition utilized for synthesis.

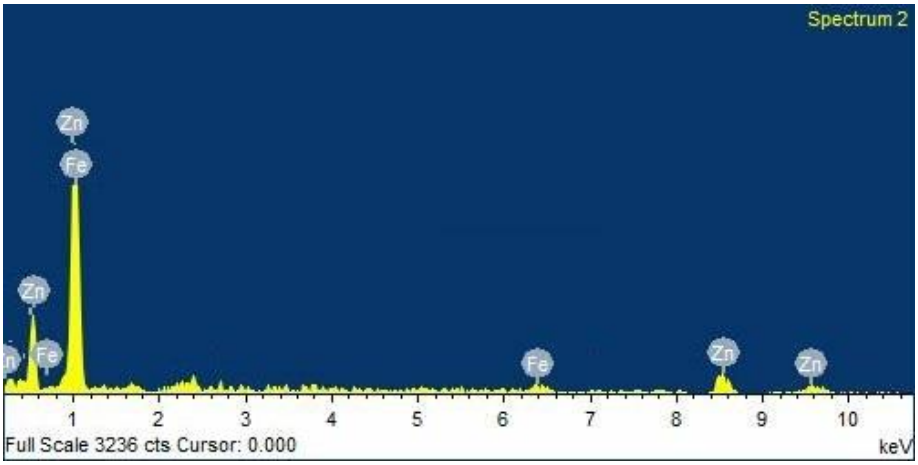

Fig.2.16. EDX of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film.

Roughness of the film were 40 to 60 nm (average 46.71 nm) as determined by 2D and 3D-AFM shown in Fig.2.17 and Fig.2.18. AFM images also confirm the wrinkle formation as visible in the depth profile of the grown film and roughness was found below 60 nm that was less than the undoped ZnO based thin film.

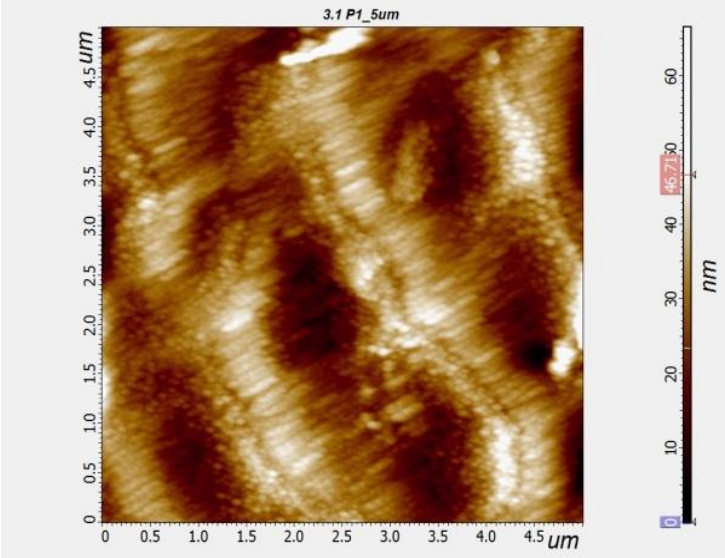

Fig.2.17. 2D-AFM of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film.

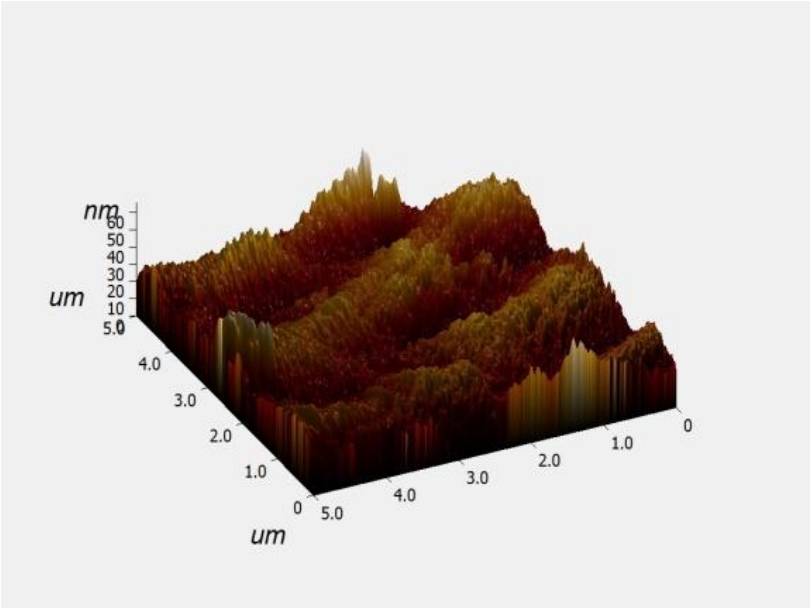

Fig.2.18. 3D-AFM of nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film.

2.4 Cu Doped Zinc Oxide Thin Film

0.65847g Zinc acetate $(CH_3COO)_2Zn\cdot 2H_2O$ **[**99.99 % Pure Powder, Sarabhai M. Chemicals] was dissolved in the 10 ml distilled water for 0.3 M solution under continuous magnetic stirring at the 35°C around one half hour till we get colorless homogeneous solution. 0.74904g Copper sulphate ($CuSO_4.5H_2O$) [99.99 % Pure Powder, Central Drug House (P) India] solution was also made by same method. Further, Copper sulphate solution added into zinc acetate solution in the ratio of doping and solution was stirrer till transparent as greenish-sky colour solution at 35 °C. Similarly, as the spin coating process .we deposited Cu doped ZnO films on the glass substrate by varying the electro-spin rpm pattern from 500 to 3000 rpm. Heating process same as previous method. Thus, we deposited $Zn_{0.92}Cu_{0.08}O$ thin film. Thickness of film was found 1.41 µm. Photograph of fabricated $Zn_{0.92}Cu_{0.08}O$ thin film sensor in Fig.2.19.

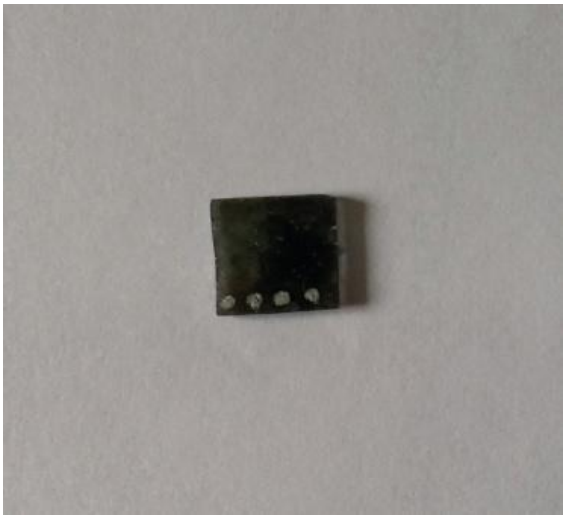

Fig.2.19. Photograph of fabricated $Zn_{0.92}Cu_{0.08}O$ thin film sensor.

The X-ray diffraction characterization suggests the poly crystalline hexagonal structure of copper doped zinc oxide thin film (JCPDS No- 36-1451) deposited on the glass substrate. Peaks are indicates the absence of impurities in the film (Fig.2.20). Peak intensities were decreased compared to undoped ZnO thin film, this may be due to the doping of 8 % copper and Cu^{+}/Cu^{2+} into host lattice without any change of structure.

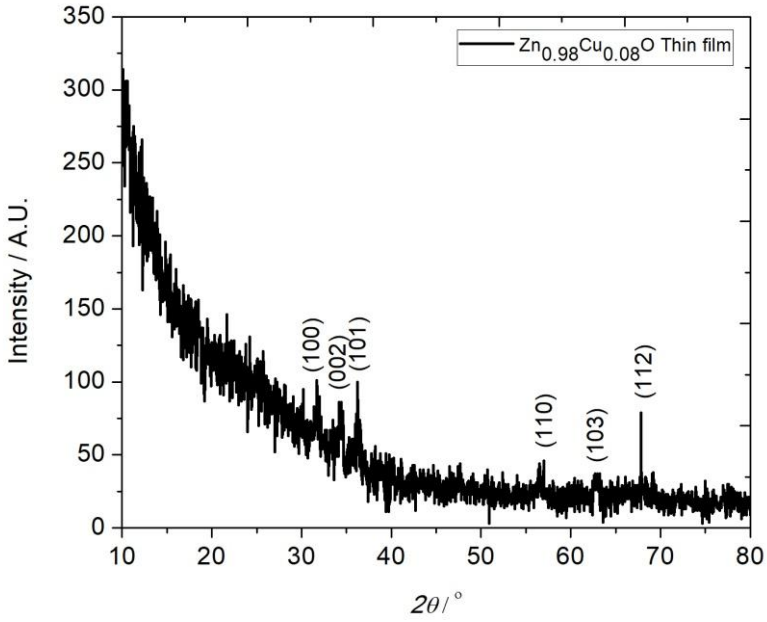

Fig.2.20. XRD pattern of $Zn_{0.92}Cu_{0.08}O$ thin film.

SEM characterization confirms that the $Zn_{0.92}Cu_{0.08}O$ thin film was uniform and smooths (Fig.2.21 and Fig.2.22). The nano-micro grains were assembled in linearly and nano-micro porous were developed in the surface. Thus, the film is suitable for formations of depletion layers at nano grain boundaries and to increase the adsorption sites. The morphology confirms the suitable for the application of gas sensing.

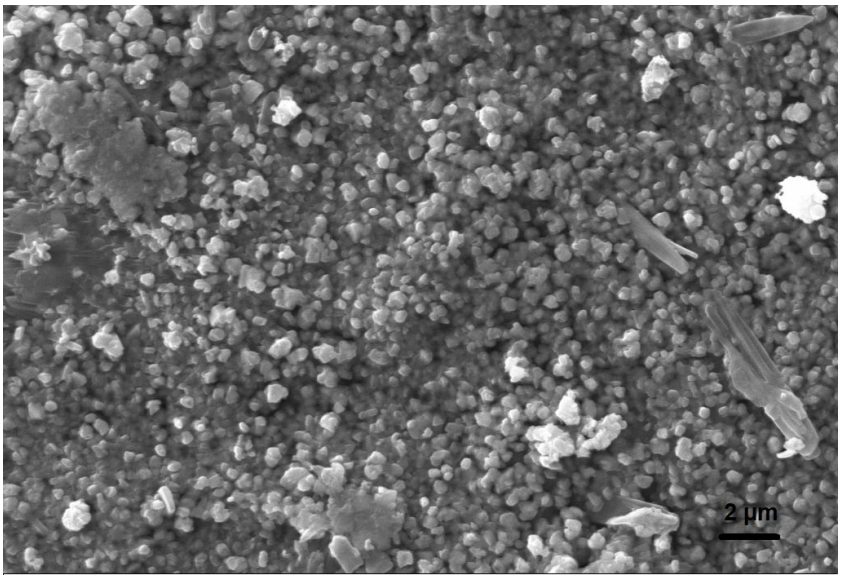

Fig.2.21. SEM of $Zn_{0.92}Cu_{0.08}O$ thin film (10.00 K X Magnification)

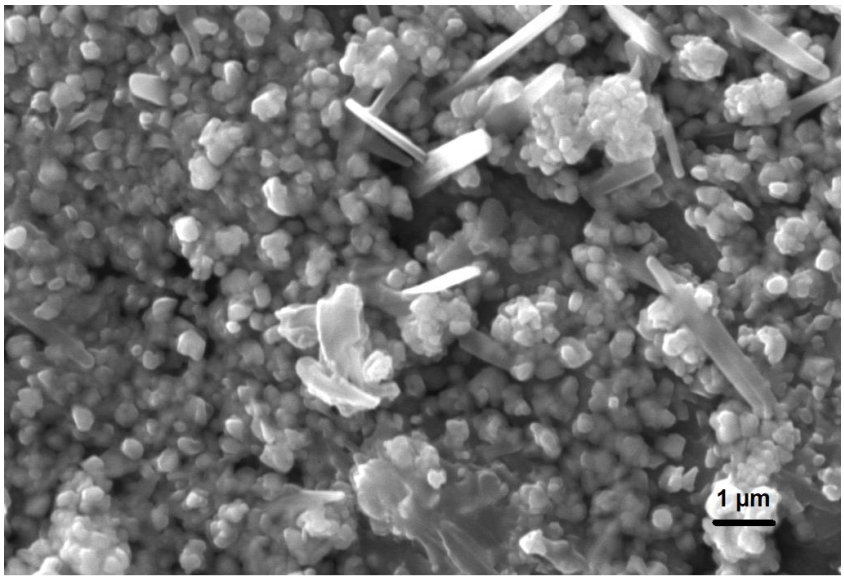

Fig.2.22. SEM of $Zn_{0.92}Cu_{0.08}O$ thin film (20.00 K X Magnification)

Fig.2.23 showed the EDX (Energy dispersive X-ray) image that verifies the compositions of the grown film. The composition of the film (Cu/Zn) is found almost same to the nominal composition utilized for synthesis.

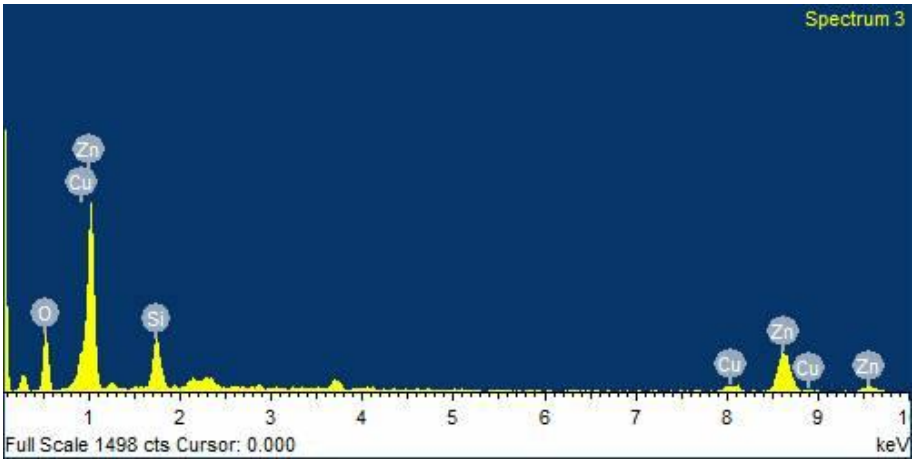

Fig.2.23. EDX of $Zn_{0.92}Cu_{0.08}O$ thin film.

Roughness of the film approximately 40 to 60 nm (average 55 nm) was determined by AFM as shown in (Fig.2.24 and Fig.2.25), 2D and 3D-AFM images also confirm the uniform and smooth surface as visible in the depth profile of the grown film and roughness is below 60 nm. The roughness is less than undoped ZnO based thin film and high than nano-wrinkled based thin film.

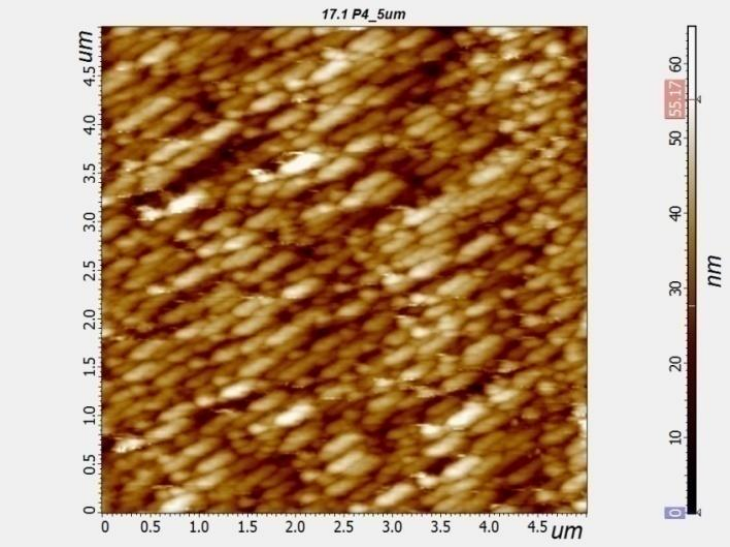

Fig.2.24. 2D-AFM of $Zn_{0.92}Cu_{0.08}O$ thin film.

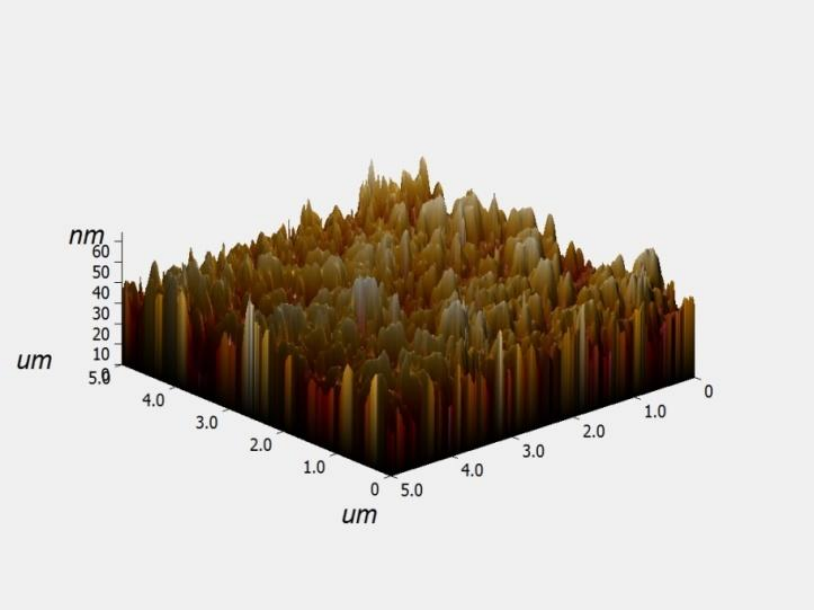

Fig.2.25. 3D-AFM of $Zn_{0.92}Cu_{0.08}O$ thin film.

2.5 Co Doped Zinc Oxide Thin Film

0.65847g Zinc acetate $(CH_3COO)_2Zn\cdot 2H_2O$ **[**99.99 % Pure Powder, Sarabhai M. Chemicals] was dissolved in the 10 ml distilled water to make 0.3 M solution under continuous magnetic stirring at the 35°C for one half hour till colorless homogeneous solution was obtained. 0.74724 g Cobalt acetate $(CH_3COO)_2Co\cdot 4H_2O$ [99.99 % Pure Powder, Sigma-aldrich] solution was also dissolved by same method. Further Cobalt acetate solution was added into zinc acetate solution in the ratio of doping and solution stirrer was till transparent pink color solution at 35 °C. Deposition of Co doped ZnO films on the glass substrate by the electro-spin rpm pattern method with continuous spinning from 500 to 3000 rpm range. Heating process same as previous method. Thickness of film was found to be 1.42 µm. Photograph of fabricated $Zn_{0.92}Co_{0.08}O$ thin film sensor in Fig.2.26.

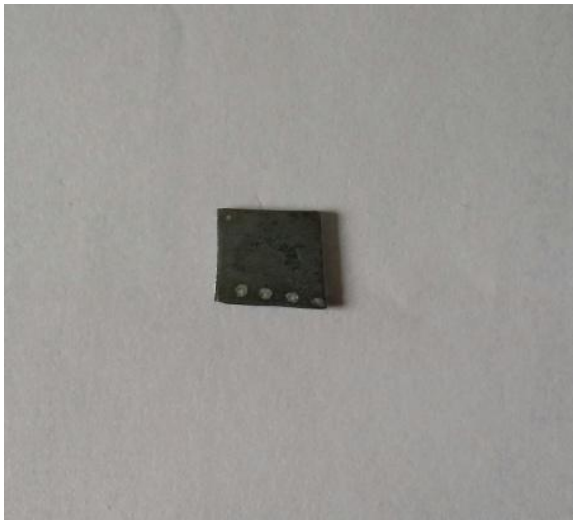

Fig.2.26. Photograph of fabricated $Zn_{0.92}Co_{0.08}O$ thin film sensor.

The X-ray diffraction characterization show the nano-crystalline hexagonal structure of cobalt doped zinc oxide thin film (JCPDS No- 36-1451) deposited on the glass substrate. Peaks were indicated to cobalt doped zinc oxide with absence of impurities (Fig.2.27) and, also peaks were of less intensities compared to undoped ZnO film due to the doping of cobalt in possibley Co^{2+}/ Co^{3+} states into host lattice of zinc oxide without any changes or modification of crystal structure.

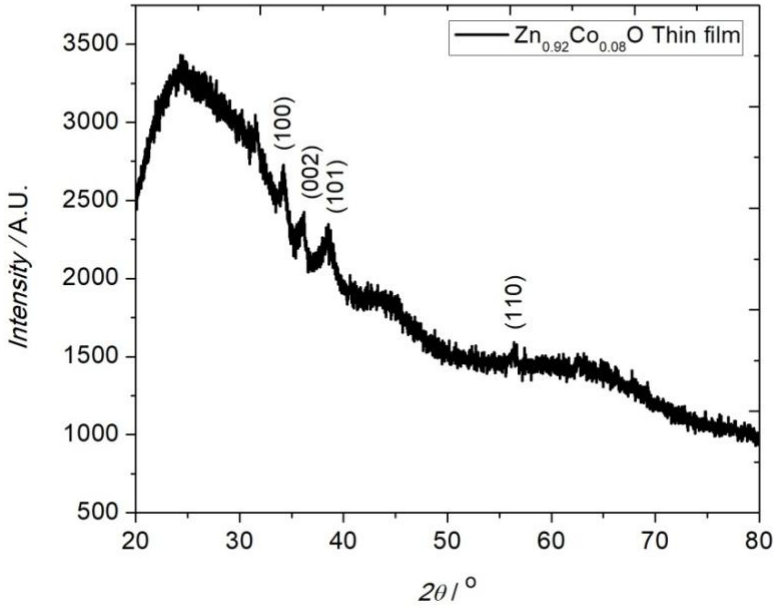

Fig.2.27. XRD pattern of $Zn_{0.92}Co_{0.08}O$ thin film.

In the SEM characterization confirmed that the $Zn_{0.92}Co_{0.08}O$ thin film was uniform and smooth (Fig.2.28 and Fig.2.29). The nano-micro grains in the form of nano balls were assembled in linearly and nano-micro porous structure at surface. The developed film was highly dense, contain fewer porous surface of thin film and Cu doped nano-crystalline thin film. The morphology confirmed to the suitability of film for application in gas sensing.

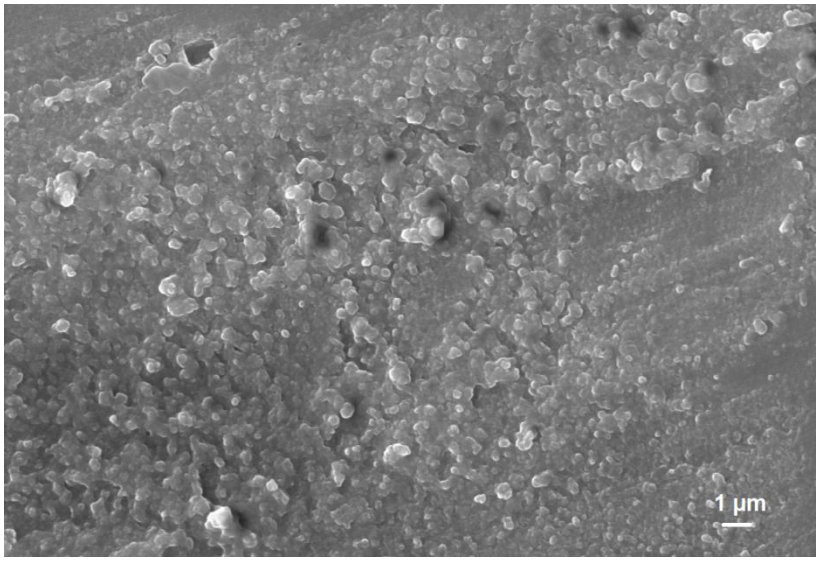

Fig.2.28. SEM of $Zn_{0.92}Co_{0.08}O$ thin film (10.00 K X Magnification)

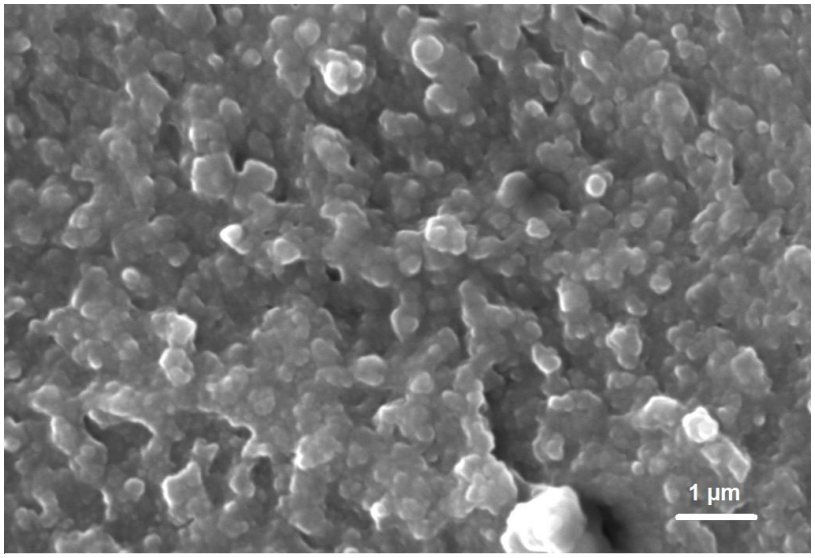

Fig.2.29. SEM of $Zn_{0.92}Co_{0.08}O$ thin film (30.00 K X Magnification)

Fig.2.30 showed the EDX (Energy dispersive X-ray) image that verifies the compositions of the grown film. The compositions of the film (Co/Zn) were found almost same to the nominal composition utilized for synthesis or fabrication of the film.

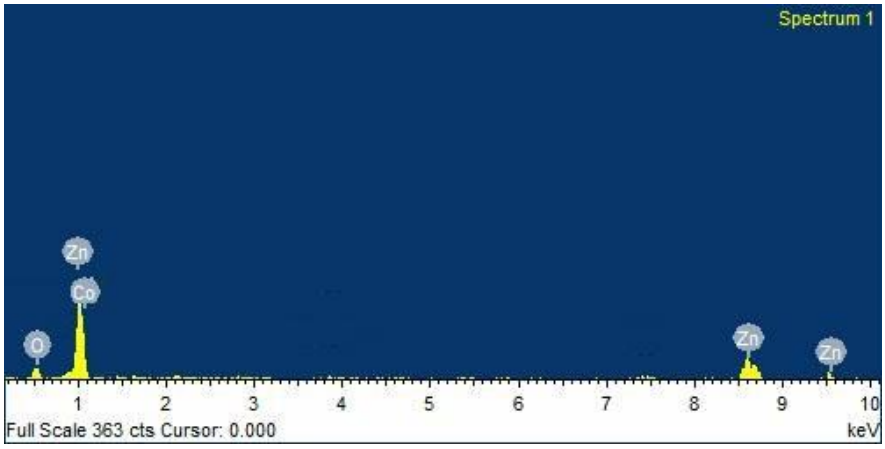

Fig.2.30. EDX of $Zn_{0.92}Co_{0.08}O$ thin film.

Roughness of the film were found in range of 90 to 160 nm (average 139 nm) as determined by AFM results (Fig.2.31 and Fig.2.32). 2D and 3D AFM images also confirmed the uniform and smooth surface as visible in the depth profile of the grown film and roughness was found below 160 nm. The roughness was high than undoped zinc oxide, nano-wrinkled and copper doped nano-crystalline.

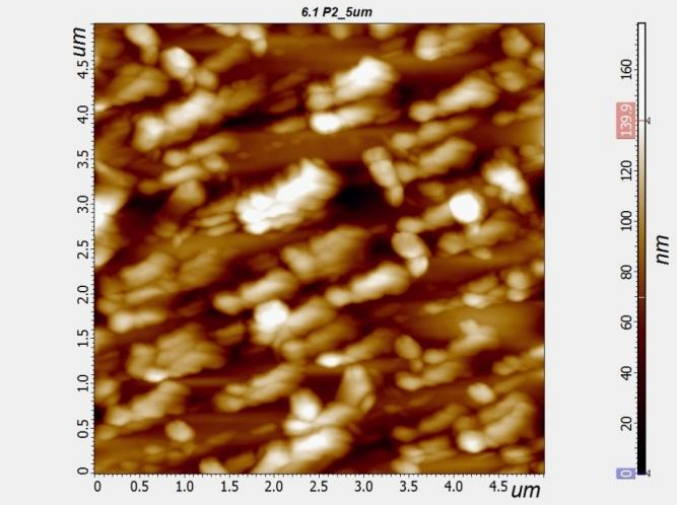

Fig.2.31. 2D-AFM of $Zn_{0.92}Co_{0.08}O$ thin film.

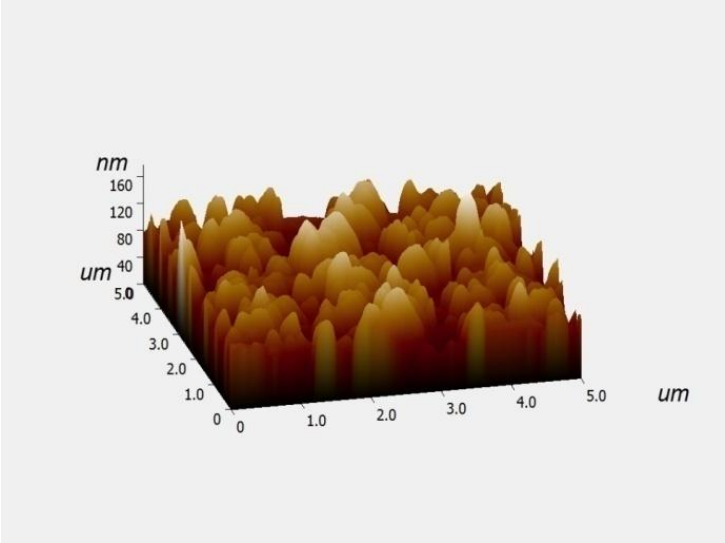

Fig.2.32. 3D-AFM of $Zn_{0.92}Co_{0.08}O$ thin film.

2.6 Ni Doped Zinc Oxide Thin Film

0.65847g Zinc acetate $(CH_3COO)_2Zn{\cdot}2H_2O$ **[**99.99 % Pure Powder, Sarabhai M. Chemicals] was dissolved in the 10 ml distilled water for to make 0.3 M solution under continuous magnetic stirring at the 35°C for one half hour till colorless homogeneous solution. 0.87243 g Nickel nitrate $[Ni(NO_3)_2.6H_2O]$ [99.99 % Pure Powder, Central Drug House (P) India] solution was also made by same method. Further Nickel nitrate solution was added into Zinc acetate solution in the ratio of doping and kept of stirrer till transparent homogeneous as slightly grass green colored solution was obtained at 35 °C. We deposited Ni doped ZnO films on the glass substrate by the electro-spin rpm pattern with varying spinning from 500 to 3000 rpm. Heating process same as previous method. Thickness of the film was found close to 1.44 µm. Fig.2.33 shows the photograph of fabricated $Zn_{0.92}Ni_{0.08}O$ thin film sensor.

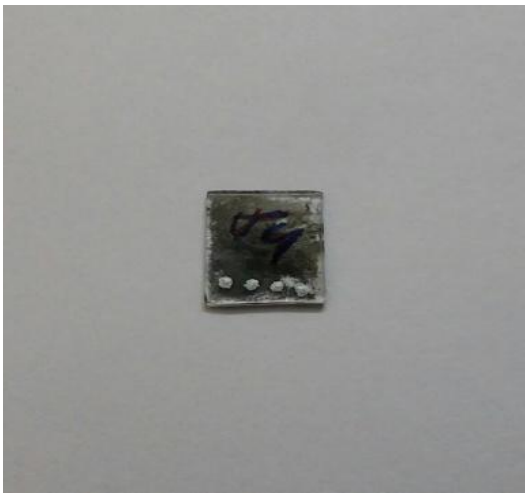

Fig.2.33. Photograph of fabricated $Zn_{0.92}Ni_{0.08}O$ thin film sensor.

The X-ray diffraction characterization shown to the nano-crystalline hexagonal structure of nickel doped zinc oxide thin film (JCPDS No- 36-1451) deposited on the glass substrate. Peaks are indicated to nickel doped zinc oxide (Fig. 2.34). Mostly is present Ni^{2+} in the host lattice of ZnO, without any changed in its crystal structure. Peak intensified were found very low suggesting partially presence of amorphous grains in the film.

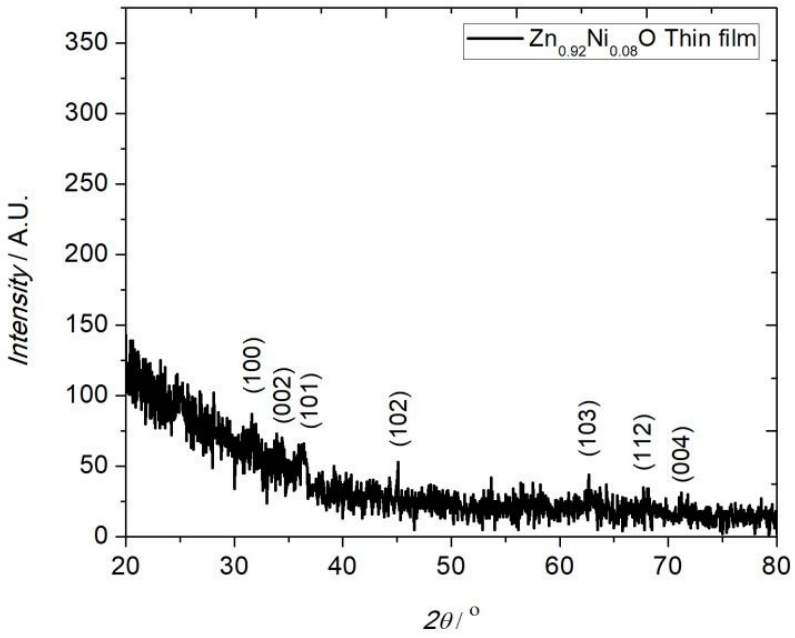

Fig.2.34. XRD pattern of $Zn_{0.92}Ni_{0.08}O$ thin film.

SEM characterizations confirm that the $Zn_{0.92}Ni_{0.08}O$ thin film was uniform (Fig.2.35 and Fig.2.36). The result also suggest that the surface densing was very high compared to undoped ZnO, nano-wrinkled $Zn_{0.92}Fe_{0.08}O$, $Zn_{0.92}Cu_{0.08}O$ and $Zn_{0.92}Co_{0.08}O$ thin films. Grown nano-micro grains, show confirmation of fewer porous in thin films. So, the formation of depletion layers somewhere at nano-micro grain boundaries increases the adsorption sites. Overall morphology confirms the suitability of film for application of gas sensing.

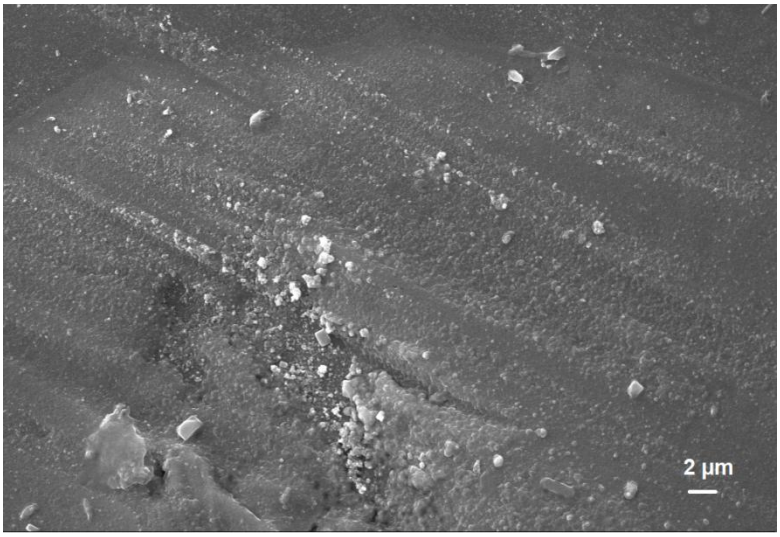

Fig.2.35. SEM of $Zn_{0.92}Ni_{0.08}O$ thin film (5.00 K X Magnification)

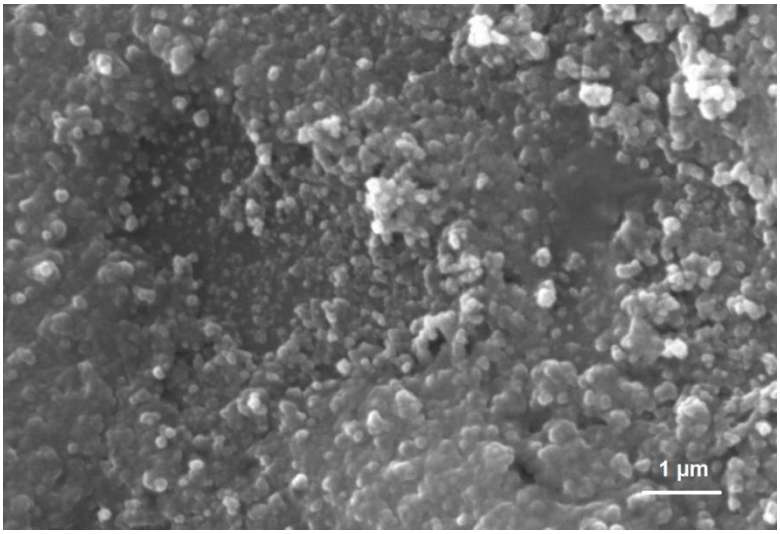

Fig.2.36. SEM of $Zn_{0.92}Ni_{0.08}O$ thin film (30.00 K X Magnification)

Fig.2.37 showed the EDX (Energy dispersive X-ray) image that confirms the compositions of the grown film. The composition of the film (Ni/Zn) was found almost same to the nominal composition utilized for synthesis.

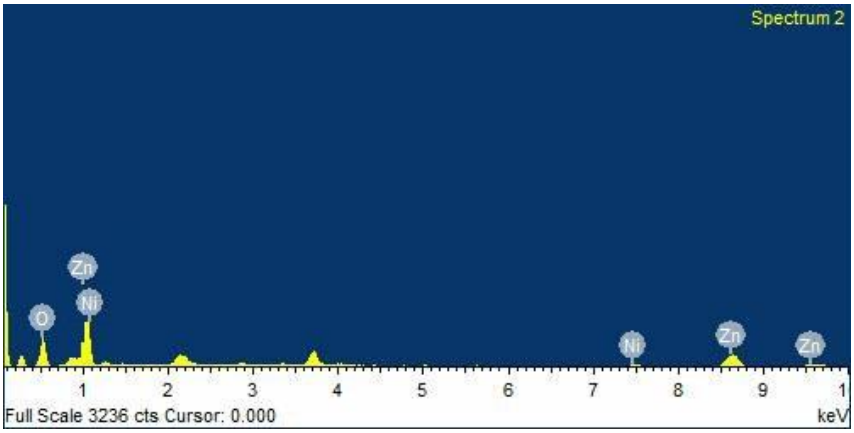

Fig.2.37. EDX of $Zn_{0.92}Ni_{0.08}O$ thin film.

Roughness of the film was found approximately in the range of 250 to 350 nm (average 322 nm) as determined by AFM (Fig.2.38 and Fig.2.39). Images of 2D and 3D AFM confirm the uniform surface as visible in the depth profile of the grown film. Smoothness of film was lower than the other types of films like as undoped ZnO flat thin film, nano-wrinkled $Zn_{0.92}Fe_{0.08}O$ thin film, $Zn_{0.92}Cu_{0.08}O$ thin film and $Zn_{0.92}Co_{0.08}O$.

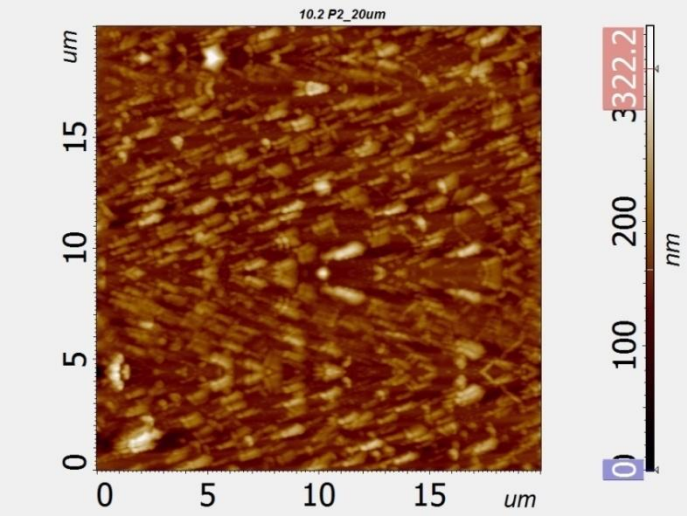

Fig.2.38. 2D-AFM of $Zn_{0.92}Ni_{0.08}O$ thin film.

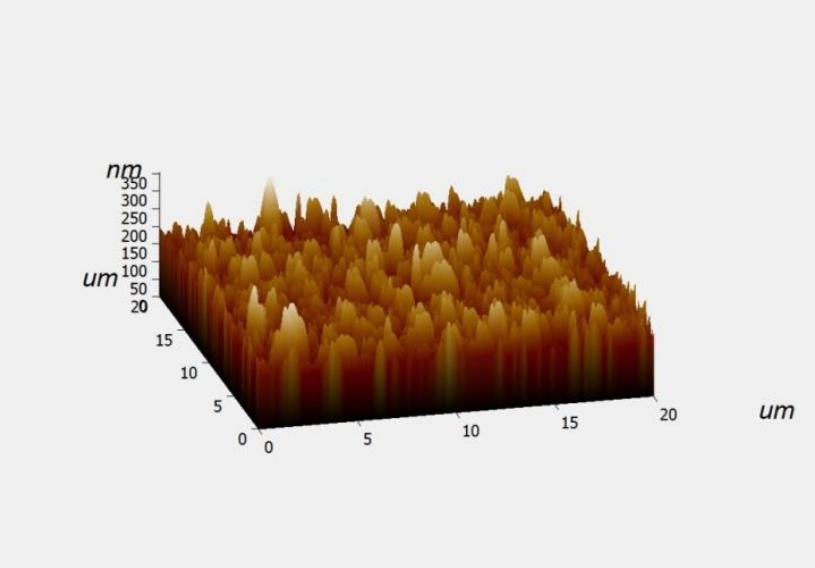

Fig.2.39. 3D-AFM of $Zn_{0.92}Ni_{0.08}O$ thin film.

2.7 Undoped Zinc Oxide (ZnO) Nano-Wired based Thin Film

Zinc acetate [$(CH_3COO)_2Zn.2H_2O$] was dissolved in 2-Methoxyethanol ($C_3H_8O_2$**)** to make 0.3 M concentration solution and stirred at 30 °C for one and half hour, thereafter diethyl amine ($C_4H_{11}N$) was added in it and solution was further stirred for one hour till solution became transparent, colorless and viscous. Drop casting was carried out at cleaned glass substrate which was on hold at spin coating machine. Substrate was spun at 2500 to 3000 rpm for 5 sec. The spun sample was kept on 250 °C at hot plate for 5 min for drying. The complete coating cycle was repeated for 5 times to get the good quality of coated film on glass substrate. After that the sample was kept into a furnace at 400 °C and, It furnace was heating start from 30 °C at 500 °C with heating rate of 5 °C/min. The sample was removed from the furnace just after temperature reached to 500 ^oC. Thickness of film was found to be 1.6 µm. Fig. 2.40 show the photograph of deposited thin film.

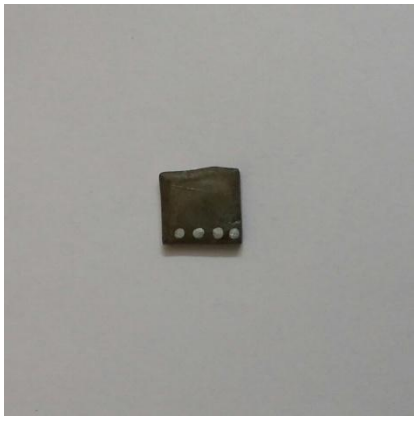

Fig.2.40. Photograph of fabricated undoped ZnO nano-wired thin film sensor.

The X-ray diffraction characterization confirmed the poly crystalline hexagonal structure of undoped zinc oxide thin film (JCPDS No- 36-1451) deposited on the glass substrate. Peaks are indicated to zinc oxide (Fig.2.41).

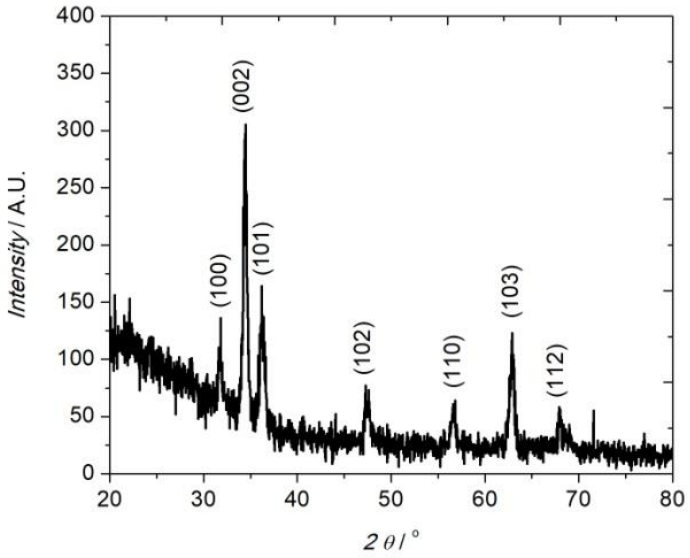

Fig.2.41. XRD pattern of undoped ZnO nano-wired thin film.

SEM characterization confirms that the undoped ZnO thin film was uniform, smooth and nano wires are coagulated in broom-sticks manner (Fig.2.42 and Fig.2.43). The nano-wired present in the film provide the specific large area for adsorption sites and it can be correlated to the improved gas sensing properties thus the film seems to be suitable for methane sensing due to formations of depletion layers at nano wires surfaces and increased to adsorption sites. The morphology approved the suitability of film or application of gas sensing.

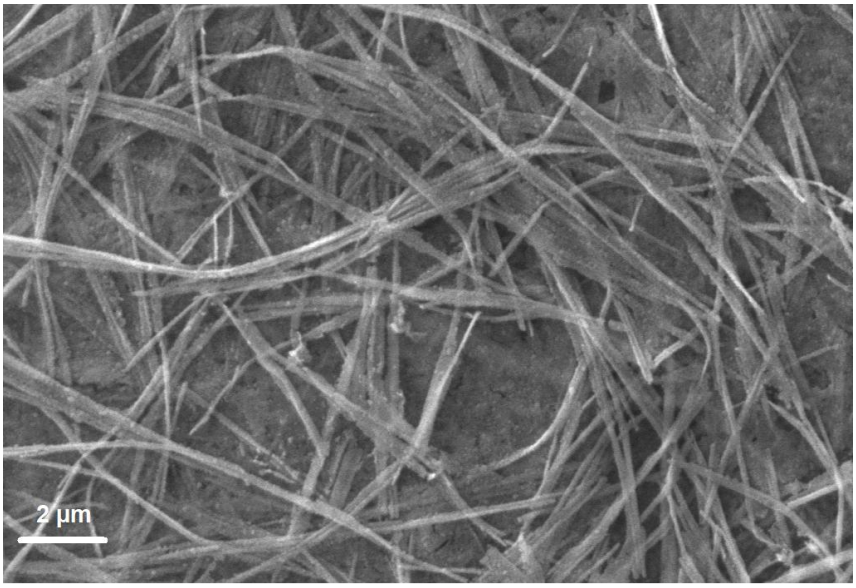

Fig.2.42. SEM of undoped ZnO nano-wired thin film (15.00 K X Magnification)

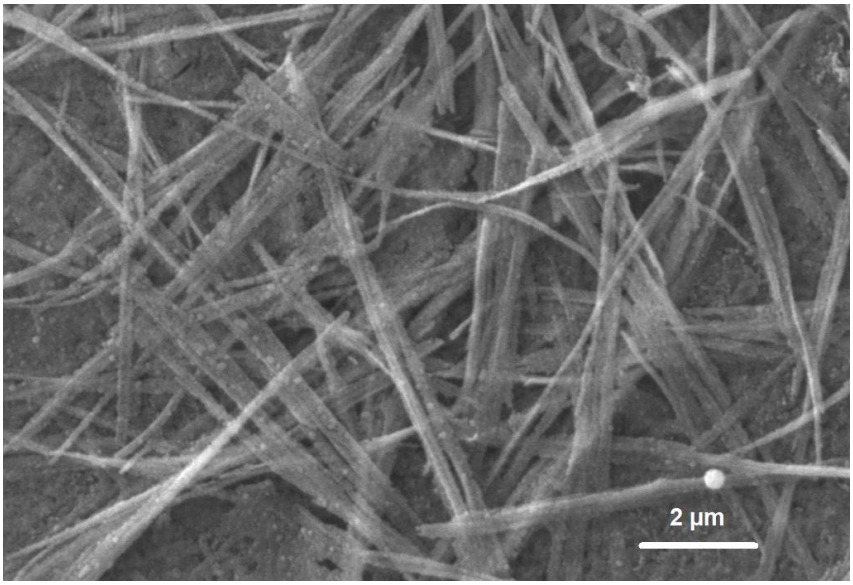

Fig.2.43. SEM of undoped ZnO nano-wired thin film (20.00 K X Magnification)

Fig.2.44 showed the EDX (Energy dispersive X-ray) image that verifies the compositions of the grown film. The composition of the film ZnO was found almost same to the nominal composition utilized for synthesis.

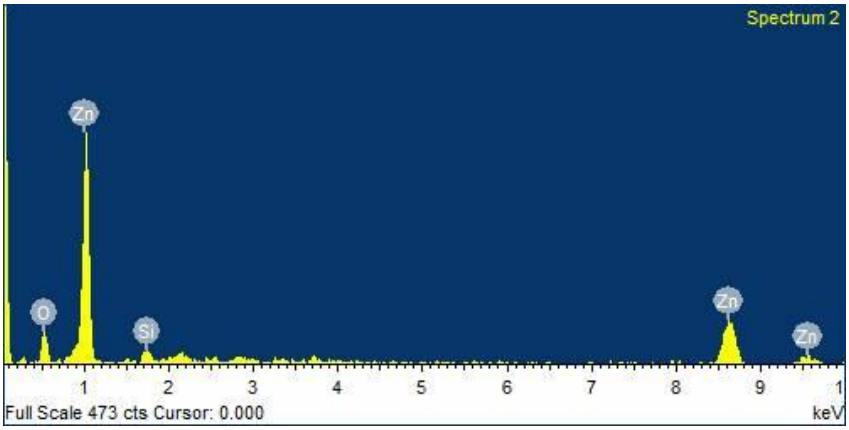

Fig.2.44. EDX of undoped ZnO nano-wired thin film.

Roughness of the film was approximately in the range of 200 to 250 nm (average 210 nm) as determined by the AFM of the film (Fig.2.45 and 2.46). 3D-AFM images also confirm the uniform and smooth surface of the film. The roughness was found higher than the undoped ZnO flat thin film, surface was found suitable for increase adsorption sites due to the gowned of nano-wires in the entire film.

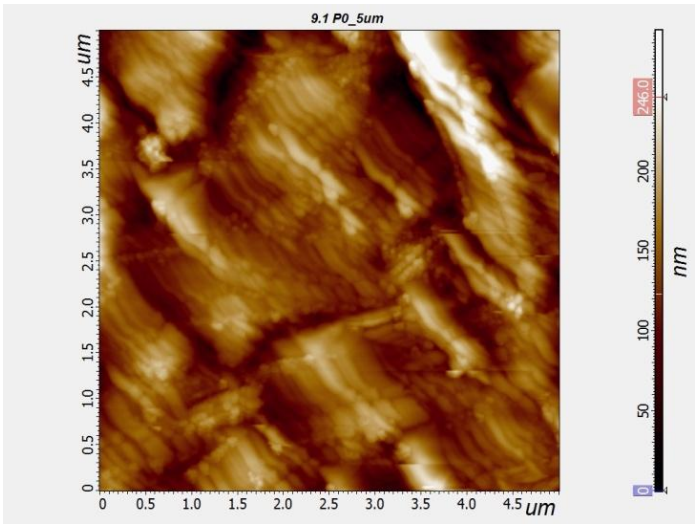

Fig.2.45. 2D-AFM of undoped ZnO nano-wired thin film.

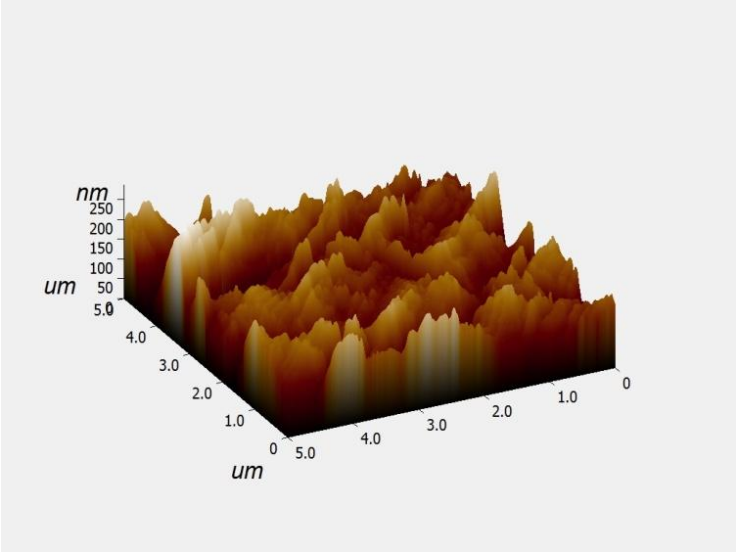

Fig.2.46. 3D-AFM of undoped ZnO nano-wired thin film.

2.8 Cu Doped Zinc Oxide ($Zn_{0.92}Cu_{0.08}O$) Nano-Strips based Thin Film

For the fabrication of $Zn_{0.92}Cu_{0.08}O$ thin films, 2.202 g Zinc carbonates ($ZnCO_3.2ZnO.3H_2O$) **[**68 % Minimum assay as ZnO**,** Purchase Central Drug House (P)] was dissolved in aqua regia solution (200 ml) and stirrer at 45°C till transparent solution of golden brown color was appeared. 0.2579 g Copper (II) sulphate ($CuSO_4.5H_2O$) [99.5 % pure powder, Purchase Central Drug House (P)] was dissolved in distilled water in other beaker. Thereafter, Copper (II) sulphate [$CuSO_4.5H_2O$] solution was transferred into Zinc carbonate solution on the hot-plate at 100°C. After 5 min continuous stirring, 7.65 g Melamine ($C_3H_6N_6$) [97.5% Pure Powder, G.S. Chemical testing Lab] was added in it. Further the solution stirred for 5 h at 100°C and color of the solution changed to slight green-bluish color. The solution was dropped on the glass substrate spinning with 2500 to 3000 rpm and holds for 5 sec. After that the deposited glass substrate was dried / heated at 250 °C on the hoted plate for 5 min. The coating cycle was repeated 5 times to get the good quality of coating. Further sample was kept into a furnace at 700 °C and, It furnace was heating start from 30 °C to 800 °C with heating rate of 5 °C/min. The sample was removed from the furnace just after temperature reached to 800 ^oC. Thickness of film was found to be 1.45 µm. Photograph of fabricated $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film sensor in Fig.2.47.

Fig.2.47. Photograph of fabricated $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film sensor.

The X-ray diffraction characterization confirms the poly crystalline hexagonal structure of copper doped zinc oxide thin film (JCPDS No- 36-1451) deposited on the glass substrate. Peaks are indicated to zinc oxide diffraction planes (Fig.2.48). Peaks intensities were are also decreased than undoped ZnO thin film due to the doping of 8 % copper into host lattice without any change of structure.

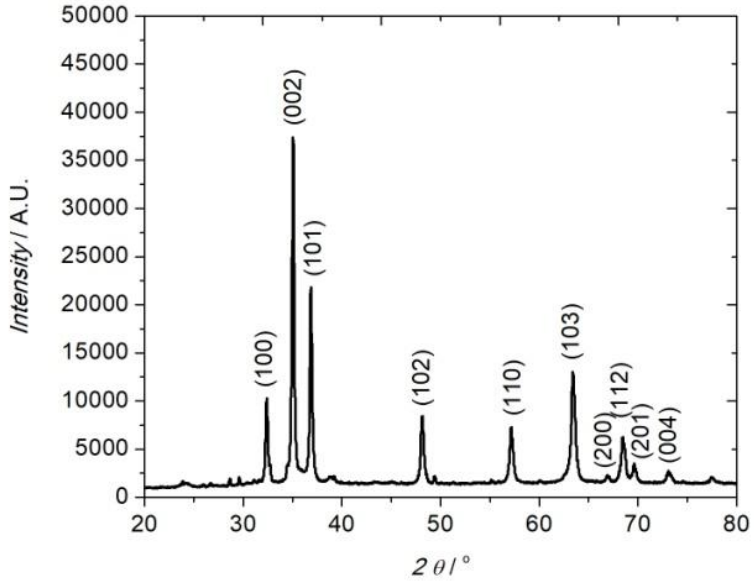

Fig.2.48. XRD pattern of $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film.

SEM characterization confirmed that the $Zn_{0.92}Cu_{0.08}O$ thin film was uniform and smoothes (Fig.2.49 and 2.50). The nano-strips were grown through the entire film and, pores were developed in the surface of the film. The presence nano-structures confirmed the increase of adsorption sites due to increase in specific areas of nano-strips surfaces (Fig.2.51). So, film seems to be suitable for formations of depletion layers at nano strips and to show increased sensitivity. The morphology of the film seemed to the suitable for applicable of gas sensing.

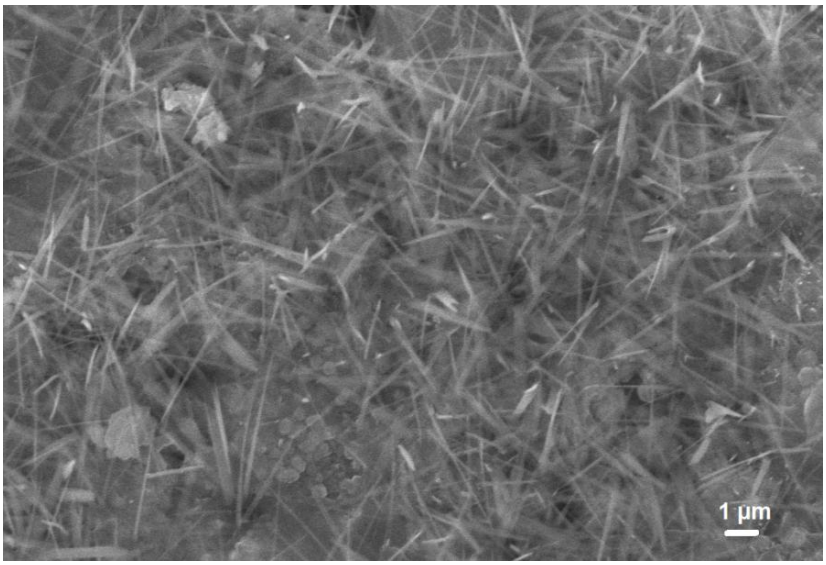

Fig.2.49. SEM of $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film (10.00 K X Magnification)

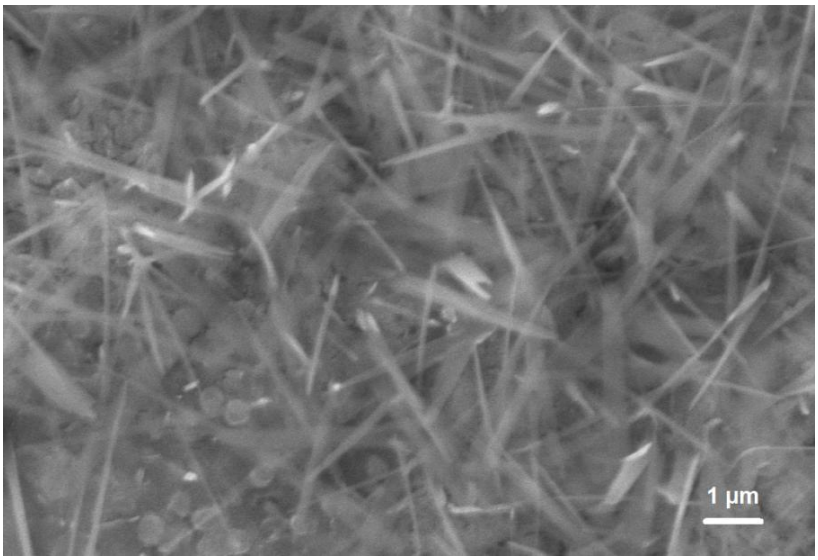

Fig.2.50. SEM of $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film (20.00 K X Magnification)

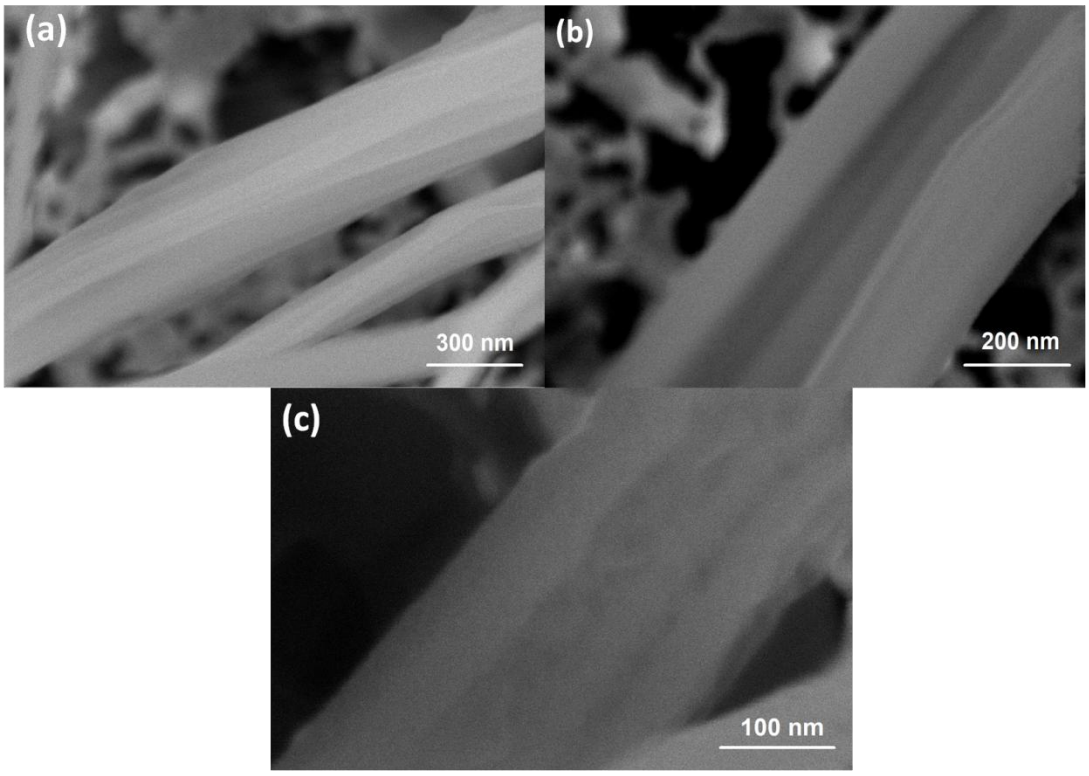

Fig.2.51 (a, b, c). HR-SEM of nano-strip in $Zn_{0.92}Cu_{0.08}O$ thin film at different magnification of nano-strip surfaces.

In Fig.2.52, showed the EDX (Energy dispersive X-ray) image that verifies the compositions of the grown film. The composition of the film (Cu/Zn) is found almost same to the nominal composition utilized for synthesis.

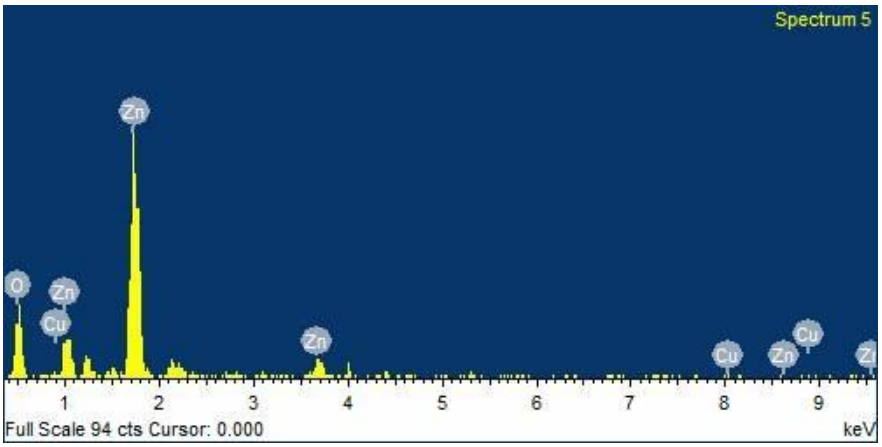

Fig.2.52. EDX of $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film.

Roughness of the film was found approximately 225 to 250 nm (average 220 nm) as determined by the AFM (Fig.2.53 and Fig.2.54). 3D-AFM images also confirm the uniform and smooth surface of the film as visible in the depth profile of the grown film and roughness was found below 300 nm. AFM study also confirms the suitability of the film for gas sensing application.

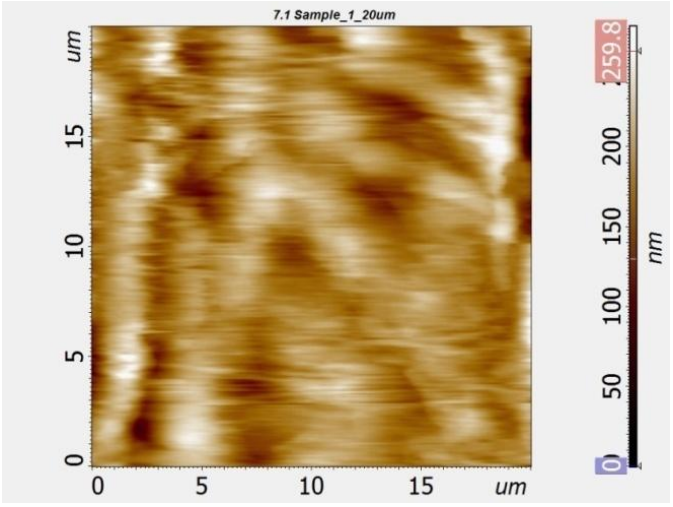

Fig.2.53. 2D-AFM of $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film.

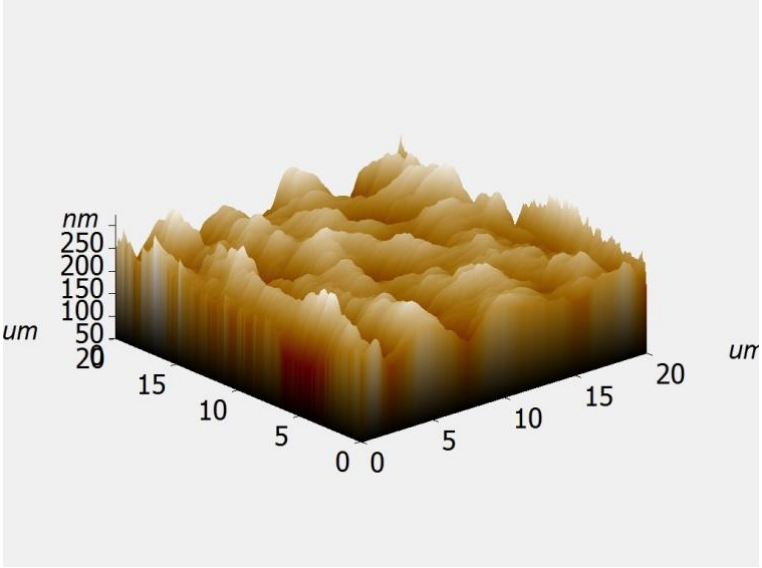

Fig.2.54. 3D-AFM of $Zn_{0.92}Cu_{0.08}O$ nano-strip thin film.

2.9 Fe Doped Zinc Oxide ($Zn_{0.92}Fe_{0.08}O$) Nano-Net based Thin Film

For the fabrication of $Zn_{0.92}Fe_{0.08}O$ thin films, 2.202 g Zinc carbonates ($ZnCO_3.2ZnO.3H_2O$) **[**68 % Minimum assay as ZnO**,** Central Drug House (P) India] was dissolved in aqua regia solution (200 ml) and stirrer at 45°C till transparent solution of golden brown color is appeared. Thereafter, 0.129 g Ferric oxide Red [Fe_2O_3, 98.5 % Pure Powder, Loba Chemie Pvt. Ltd. India.] solution was dissolved into Zinc carbonate solution on the hot-plate at 120°C. After 5 min continuous stirring, 7.65 g Melamine ($C_3H_6N_6$) [97.5% Pure Powder, G.S. Chemical testing Lab] was added in it. Further the solution stirred for 5 h at 120 °C and color of solution was changed to slight yellow-reddish color. The solution was dropped on the glass substrate spinning with 2500 to 3000 rpm and holds for 5 sec. After that the deposited glass substrate was dried / heated at 250 °C on the hot plate for 5 min. The coating cycle was repeated 5 times to get the good quality of coating. Further sample was kept into a furnace at 700 °C and, It furnace was heating start from 30 °C at 800 °C with heating rate of 5 °C/min. The sample was removed from the furnace just after

temperature reached to 800 ^{o}C. Thickness of film was found to be 1.5 µm. Photograph of fabricated $Zn_{0.92}Fe_{0.08}O$ nano-net thin film sensor in Fig.2.55.

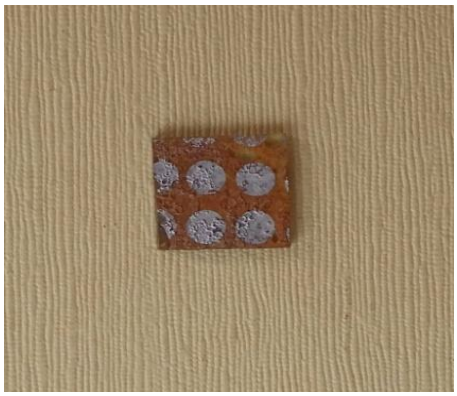

Fig.2.55. Photograph of fabricated $Zn_{0.92}Fe_{0.08}O$ nano-net thin film sensor.

The X-ray diffraction characterization confirmed the poly crystalline hexagonal structure of iron doped zinc oxide thin film (JCPDS No- 36-1451) deposited on the glass substrate. Peaks are indicated to zinc oxide diffraction peaks (Fig.2.56). Peak intensities were lower compared to undoped ZnO thin film this may be due to the doping of 8 % Iron into host lattice without any change of its crystal structure.

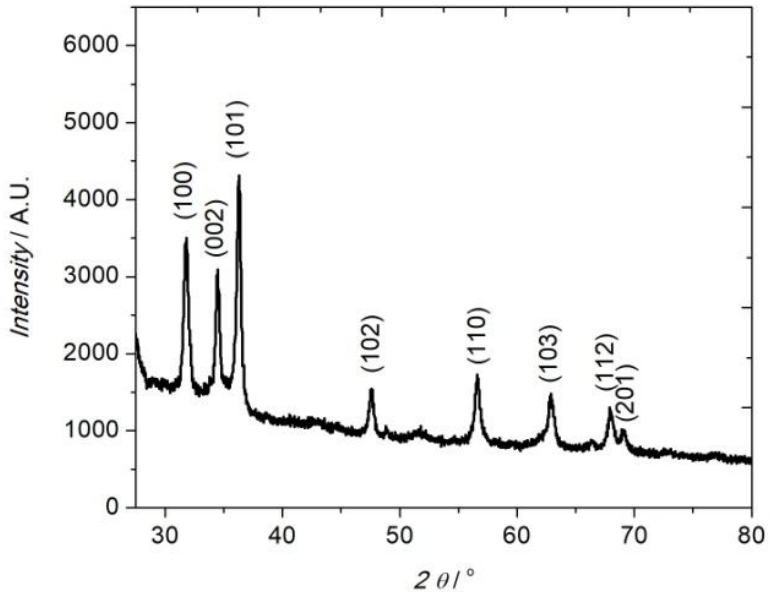

Fig.2.56. XRD pattern of $Zn_{0.92}Fe_{0.08}O$ nano-net thin film.

SEM characterization confirmed to the $Zn_{0.92}Fe_{0.08}O$ thin film was uniform (Fig.2.57 and 2.58). The nano-micro grains were assembled in uniformity; nano-micro porous were developed at grain boundaries and nano-net like spikes were grown on the grains surface. So, the porosity of film increased and became suitable for formation of depletion layer at grain boundaries and nano-net network in the ambient atmosphere. The morphology of the developed film appeared to be suitable for the application of gas sensing.

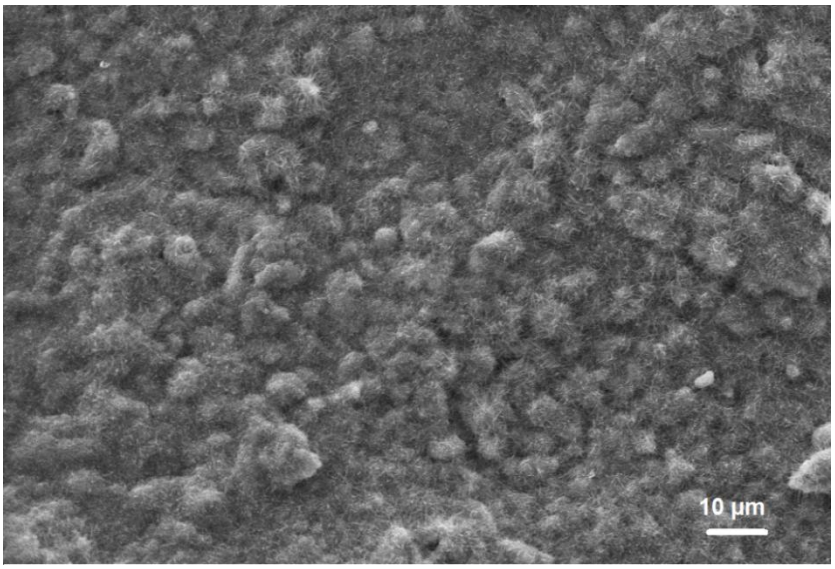

Fig.2.57. SEM of $Zn_{0.92}Fe_{0.08}O$ nano-net thin film (2.00 K X Magnification)

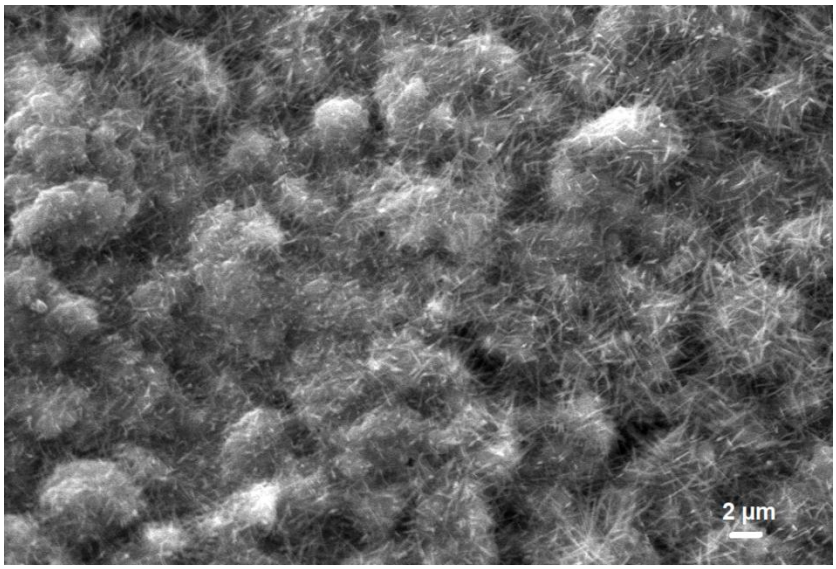

Fig.2.58. SEM of $Zn_{0.92}Fe_{0.08}O$ nano-net thin film (5.00 K X Magnification)

Fig.2.59, show the EDX (Energy dispersive X-ray) image that verified the compositions of the grown film. The composition of the film (Fe/Zn) is found almost same to the nominal composition utilized for synthesis.

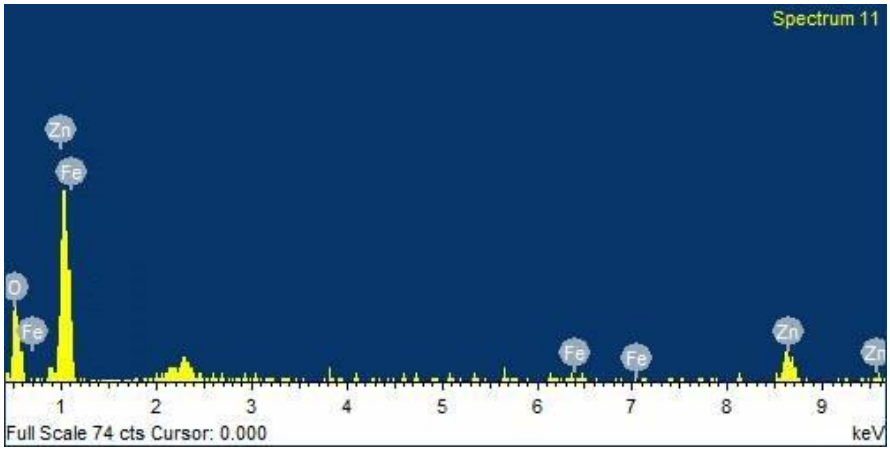

Fig.2.59. EDX of $Zn_{0.92}Fe_{0.08}O$ nano-net thin film.

Roughness of the film was found approximately 600 to 800 nm (average 721 nm) as determined by AFM study (Fig.2.60 and Fig.2.61). 3D-AFM images also confirmed the uniform and porous surface as visible in the depth profile of the grown film and roughness was found below 900 nm. the roughness was more than undoped ZnO nano-wire based thin film and $Zn_{0.92}Fe_{0.08}O$ nano-strip based thin films.

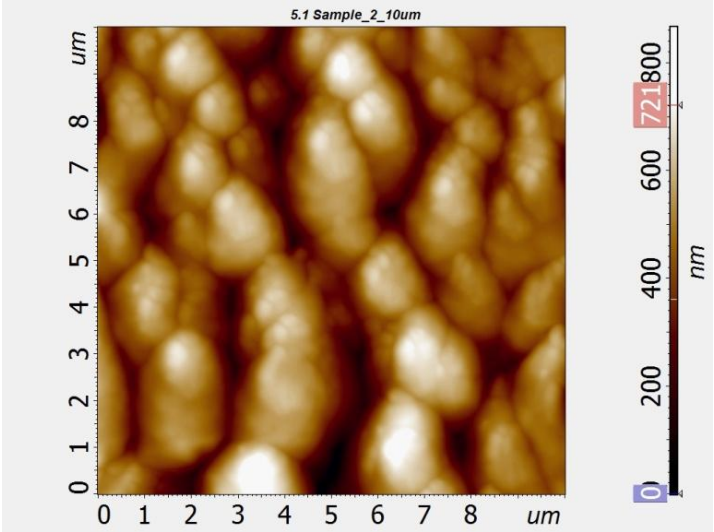

Fig.2.60. 2D-AFM of $Zn_{0.92}Fe_{0.08}O$ nano-net thin film.

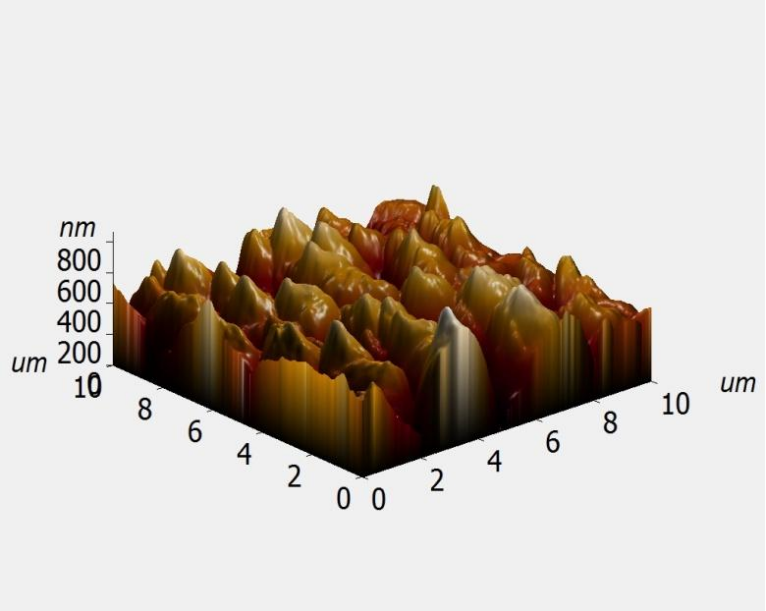

Fig.2.61. 3D-AFM of $Zn_{0.92}Fe_{0.08}O$ nano-net thin film.

2.10 Conclusion

Fabrication of undoped and 8 % Fe, Cu, Co, Ni doped ZnO based thin film on glass substrate using the technique of spin coating with rpm pattern 500 – 3000 rpm, via chemical route successfully and characterization by XRD, SEM, HR-SEM (for Fe doped nano-wrinkled film), EDX, AFM. Similarly fabrications of undoped ZnO nano-wired, 8 % Cu doped ZnO ($Zn_{0.92}Cu_{0.08}O$) nano-strips and 8 % Fe doped ZnO ($Zn_{0.92}Fe_{0.08}O$) nano-net based thin films on glass substrate using the technique of spin coating with rpm pattern 2500 – 3000 rpm, via chemical route successfully was demonstrated and characterization by XRD, SEM, EDX, AFM for deposited films and HR-SEM applied in the analysis of nano-strip surface in $Zn_{0.92}Cu_{0.08}O$ thin film.