JOURNAL OF AERONAUTICAL MATERIALS
ISSN: 1005-5053

Vol. 43, Issue-01, 2023
pp. 1673-1681

EFFECT OF ANNEALING ON STRUCTURAL AND MORPHOLOGICAL CHARACTERISTICS OF PURE AND COBALT DOPED ZINC OXIDE THIN FILM

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Abstract:

Cobalt-doped ZnO thin films have been successfully prepared using Sol-gel dip-coating technique. This work reports an investigation of the structural and morphological of ZnO particles doped with Cobalt (Co).The effect of cobalt incorporation on structural and morphological properties was investigated using X-ray diffraction [XRD] for structural studies, and Scanning Electron Microscopy [SEM] to study the morphological characteristics. The morphological studies show that the concentration of the Co dopant increases the inter-molecular space decreases and the molecules become closer thus the conductivity increases and it also favours the ferromagnetic property of ZnO. It exhibits a hexagonal structure. The obtained result proves that the ZnO pure and doped thin films elaborated by the sol-gel dip-coating technique can be used in wave guide and Transparent Conducting Oxides (TCO) solar cells.

Introduction:

Nanotechnology operates at the atomic, molecular, or macromolecular levels, in a length scale of 1-100 nanometers. The properties of materials can be different at the nanoscale for two main reasons. Nanomaterials have a relatively larger surface area when compared to the same mass of material produced in larger forms. This can make materials more chemically reactive (in some cases materials that are inert in their larger form are reactive when produced in the nanoscale form) and affect their strength or electrical properties. Quantum effects can begin to dominate the behavior of matter at the nanoscale particularly at the lower end affecting the optical, electrical magnetic behavior of materials.

Zinc oxide (ZnO), a direct and wide band gap (3.37 eV) II-VI oxide semiconductor has high exciton binding energy (nearly 60 meV at room temperature), good transparency, and long-term stability. It has been given due importance because of its excellent optoelectronic, sensing, and piezoelectric properties. It finds various technological applications like sensors, light emitting diodes, lasers, solar cells, resistive switching devices, photocatalysts, and most recently in spintronics, etc. Diluted magnetic semiconductors (DMS) formed by doping a semiconductor with a small concentration of transition metals have attracted considerable attention due to their possible applications in spintronics devices in which both spin and charge of the electrons can be used and have the potential for various technological advancements like non-volatility, increased data processing speed, decreased electronic power consumption, and increased integration densities as compared to the conventional semiconductor devices. The realization of such DMS is still a widely discussed issue due to the questionable magnetic

behavior of the material. Optical properties such as absorption and photoluminescence can enhance the understanding of the mechanisms of high-temperature ferromagnetism in transition metal doped Zinc oxide.

As a dopant, Cobalt is able to modulate both the optical and magnetic behavior of Zinc Oxide due to its abundant electron states. Its ionic radius as well as its divalent state ensures a high solubility in ZnO due to which it has been widely used for tuning the optical as well as the magnetic behavior of ZnO.

Materials and Methods:

Zinc Acetate ($C_4H_6ZnO_4$), Cobalt Acetate (Co $(C_2H_3O_2)_2$), Ethanol (C_2H_6O), and Mono Ethanol Amine (MEA) were purchased and used without any purification. The chemicals used are of laboratory-grade purity. The apparatus used are Magnetic stirrer, Glass beakers, Glass slides, Deionised water, Hot Air oven, etc. Pour ZnAc into ethanol and stir the solution for 30 minutes. After 30 minutes, a milk white solution will be obtained to that, add MEA into it. Now it turns into a clear solution of Zinc Acetate ($C_4H_6ZnO_4$).

Nanoparticles of Zn were synthesized by heating metal acetates in organic solvent following the Sol-gel dip-coating procedure. For each concentration of Co, the samples were annealed in air. The sol-gel was prepared by the dissolution of zinc acetate dihydrate in ethanol and monoethanolamine (MEA). The molar ratio of MEA to ZnAc was 0.5M. The thin films were deposited on a glass substrate by dip coating technique. After each layer deposition, the gel film was stabilized by pre-heating in the air for 10 minutes at 100°C. The procedure was repeated 30 times. The stabilized films were then crystalized by post-heating for 4 hrs at 450°C. Finally, cobalt-doped crystallized thin films with different concentrations are obtained. ZnAc and Co thin films were fabricated on HIMEDIA glass slides (CG002) by using the sol-gel technique for prescribed concentrations. Here Sol-Gel Dip-Coating technique is used in which two or more molecules combine upon the separation of water or some other simple substance to form a colloid, a system composed of solid particles dispersed in a solvent. The Sol then evolves towards the formation of an inorganic network containing a liquid phase. For the synthesis of Co-doped ZnO Nano-powder 0.5 M concentration of cobalt acetate was added into the zinc solution after adding MEA solution and the same process was repeated to obtain the Co-doped ZnO nanoparticles. The Cobalt Acetate used here is Granted Regent, and it is highly pure. The samples were further characterized to analyze the effect of cobalt doping on the properties of nanoparticles at different concentrations such as 0.5%, and 1.5%. The content of Co as the dopant was measured using electronic balance and added into the clear solution now stirs it for 2 hours at 60°C. Allow for constant stirring for 2 hours after that cover the solution with aluminium foil and allow for aging.

After aging for 24 hours start the dipping process. In this stage the technique used is the sol-gel technique, Dip the desired slides into the solution for some time then take it and hold until the extra solution gets down. This is doing because to avoid uncontrollable thickening. The main disadvantage of this process is the thickness of the thin film is uncontrollable. After dipping ten times allow it to dry by using a hot air oven for 10 minutes at

100°c, then repeat the same dipping process and finally dry it. Now the film will be well coated. Then annealing is taking place at 450°c for hours. Now the cobalt-doped zinc oxide thin film is obtained.

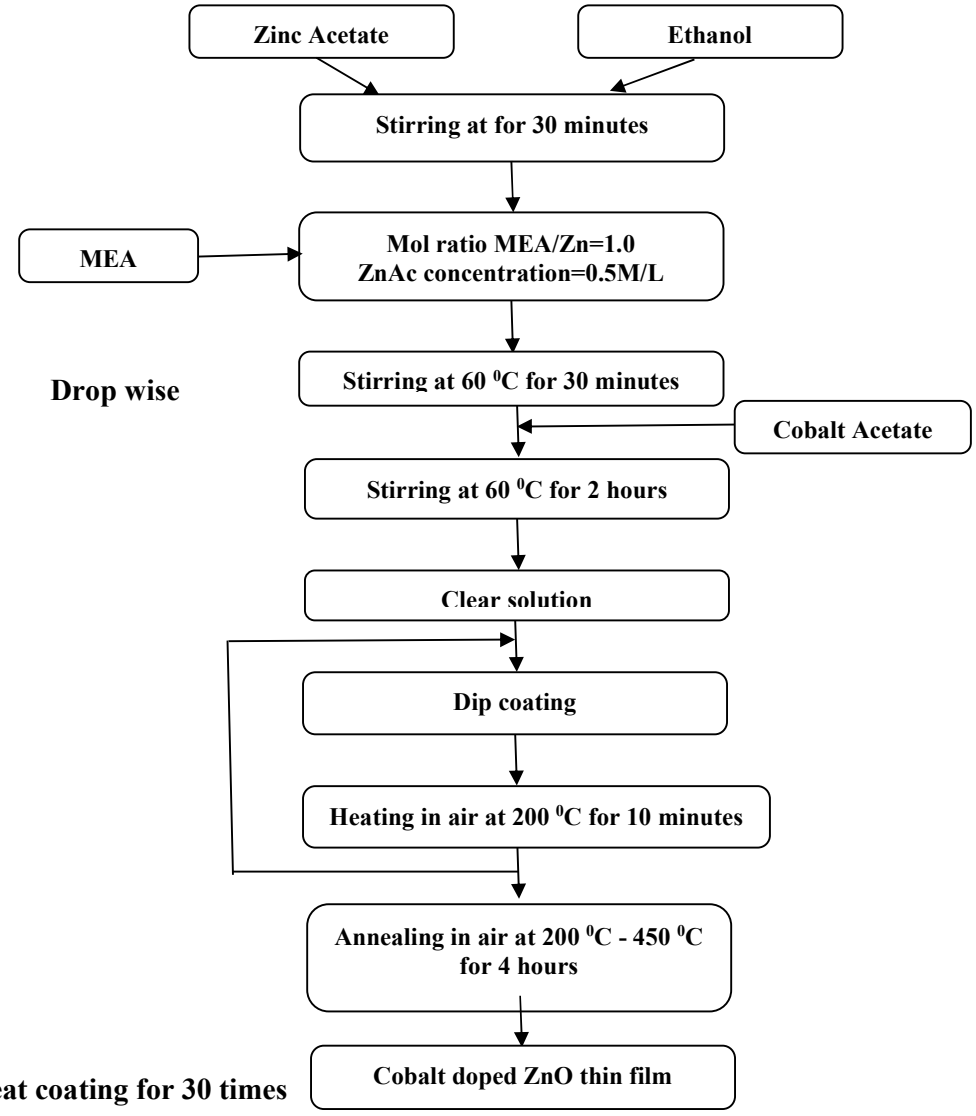


FIGURE 1.1 Flowchart for the development of Co-doped Zinc Oxide thin films preparation.

Figure 1.2 Cobalt doped ZnO solution

Results and Discussion:

X-Ray Diffraction (XRD):

XRD was used to investigate the crystal structures of the films. The crystal structure of the as deposited Zn film was hexagonal with (002) preferred orientation. When the Zn particles were oxidised to ZnO, their peaks changed considerably. The (101), (002), and (100) peaks of ZnO appeared in the diffraction patterns of the particles oxidised under applied magnetic fields of both 0 and 6 T. Several peaks of Zn still remained, but they differed between the oxidised samples. For the ZnO formed without an applied magnetic field, only the (101) peak of Zn obviously remained. Meanwhile, for ZnO oxidised under an applied magnetic field of 6 T, the (100), (101), (102), and (103) peaks of Zn were still visible. This means that the oxidation of Zn was not complete under a 6 T magnetic field, which is because a Lorentz force from the high magnetic field acted on the oxygen ions. As a result, a high magnetic field suppresses the oxidation of Zn. Additionally; the preferred orientations of ZnO particles are also different. ZnO formed without an applied magnetic field has (002) preferred orientation, while those for the sample oxidised under a magnetic field of 6 T are (101) for ZnO and (101) for Zn. In contrast, the Co-doped ZnO films did not contain Zn peaks in their XRD patterns, and the peak positions were consistent with the hexagonal wurtzite crystal structure. Furthermore, the preferred orientations for both films were (101). Because the Co content of the film was slightly increased under the high magnetic field, the peak position shifted to a higher angle, which decreased the lattice parameter c. The Co-doped ZnO films oxidised under magnetic fields of 0 and 6 T exhibited c of 0.5195 and 0.5180 nm, respectively. Additionally, the full width at half-maximum (FWHM) of the three strongest peaks for the films oxidised under magnetic fields of 0 and 6 T were 0.73 ± 0.06° and 0.76 ± 0.03°, respectively. The grain sizes in these films were then calculated from their FWHM to be 11.84 ± 0.9 and 11.42 ± 0.7 nm for the films oxidised under magnetic fields of 0 and 6 T, respectively. This suggests that the grain sizes of

both films are similar, even though AFM indicated that the surface particle size of the film oxidised under a magnetic field of 6 T was larger than that of the film oxidised without an applied magnetic field.

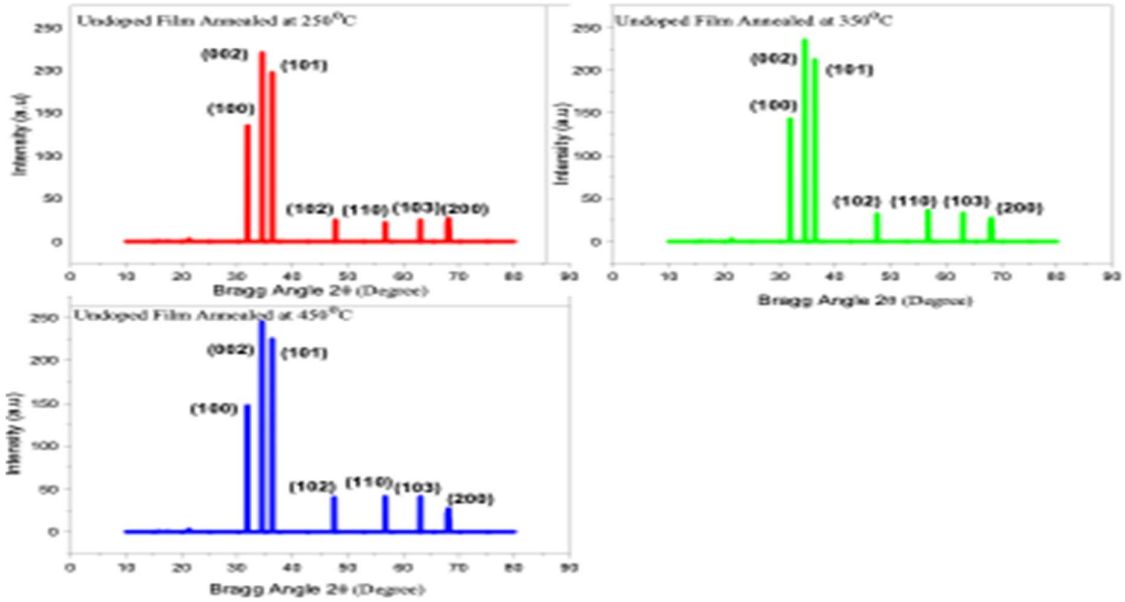


Fig 2.1 XRD for pure ZnO thin film

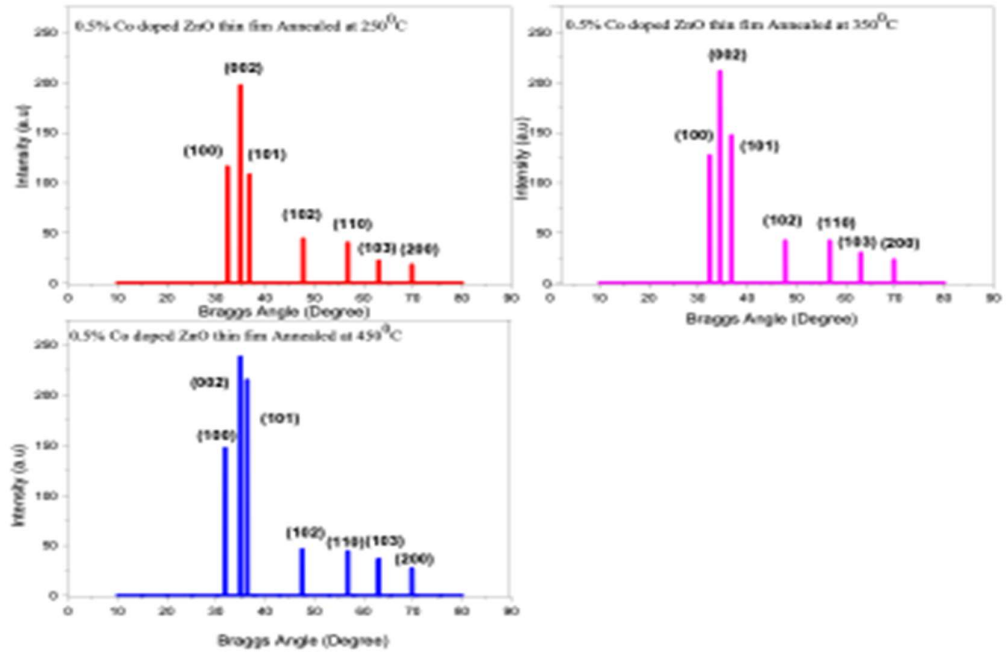


Fig 2.2 XRD for0.5%Co doped ZnO thin film

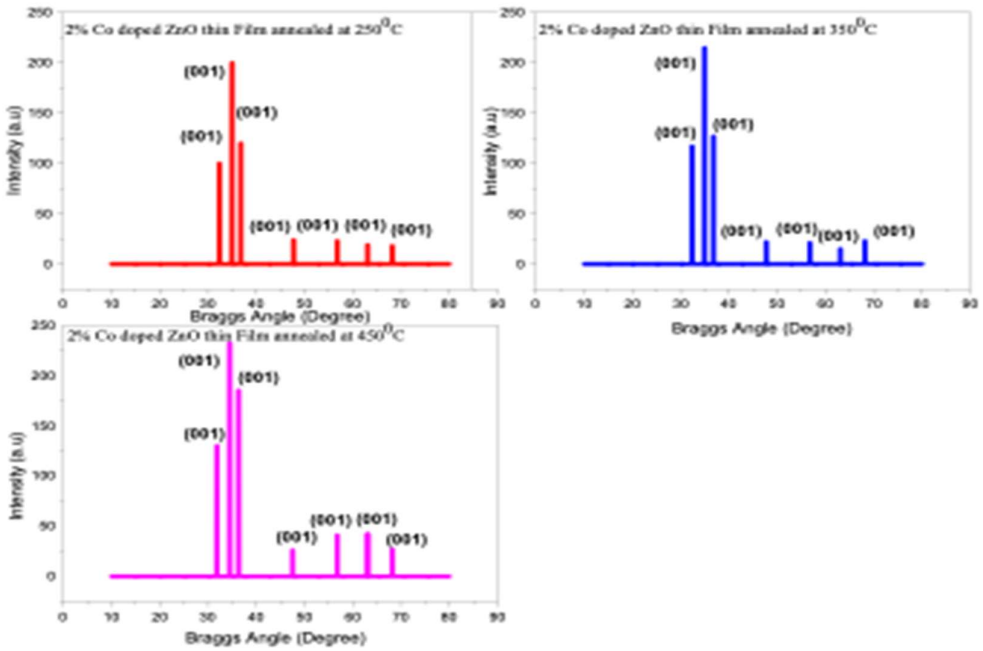


Fig 2.3 XRD for1.5%Co doped ZnO thin film

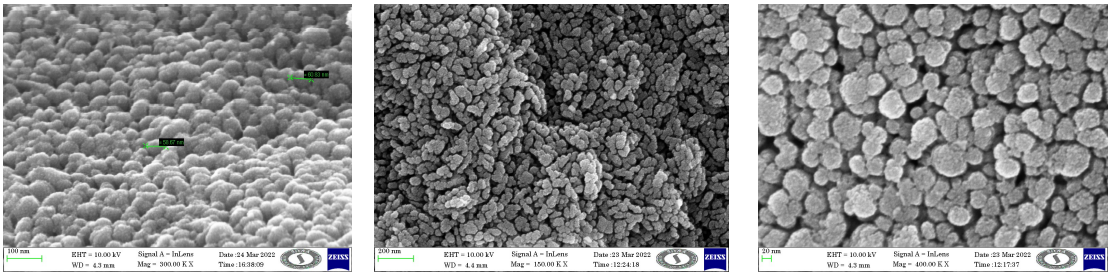
The XRD pattern of the thin film shows a dominating peak (002), indicating a high preferential x-axis-oriented wurtzite-type crystalline structure and polycrystalline with grains uniformly perpendicular to the surface substrate. The peaks occur at the range between 32°-37°. The energy band gap increases from 3.23 – 3.37 eV with increasing Co doping. The obtained result proves that the ZnO pure and doped thin films elaborated by the sol-gel dip coating technique can be used in wave-guiding and TCO for solar cells etc.

Scanning Electron Microscope (SEM):

A typical SEM image of pure ZnO and Cobalt doped (different concentrations) ZnO thin films respectively, on glass substrates at 450°C with dip coating technique. The surface is smooth and the crystallites are fine. No big particles can be found in the SEM images. The grain size is (30-100) nm. It is found that the concentration of Cobalt doped has a significant effect on the ZnO film surface structure. The grain size increases with the increase in the dopant concentration. The SEM image shown here gives a clear idea about the grain size, intermolecular space and structure. The addition of Co makes a significant change in the morphology of the ZnO thin film.

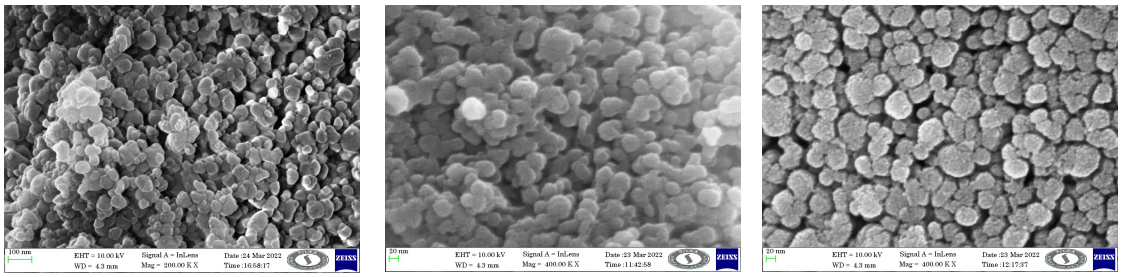
The surface morphology of films was studied using SEM, and the bottom views SEM images were taken at the same magnifications. It is observed that the pure ZnO thin film has a grain size slightly lesser than that of the doped ones, it ranges between 30-50 nm. As coming to **0.5%** Cobalt doped thin film the grain size increases to the range 50-70 nm and for **1.5%** Cobalt doped thin films it ranges from 90-110 nm respectively. Also observed is that the molecules are loosely packed in the pure one and the intermolecular space decreases as the

dopant concentration increases. **0.5%** and **1.5%** Cobalt doped ZnO thin film displayed in the above figure indicate the presence of hexagonal-shaped grains.



(a) (b) (c)

Fig 3.1(a), (b), (c) SEM Image for 0.5% at annealing temperature 250°C, 350°C, 450°C respectively



(a) (b) (c)

Fig 3.2(a), (b), (c) SEM Image for 1.5% at annealing temperature 250°C, 350°C, 450°C respectively

Conclusion:

ZnO has some unique properties and some advantages over other wide gap materials such as GaN which is widely used today to produce short wavelength light emitting devices. ZnO materials have potential applications in optoelectronics, such as light-emitting diodes and laser diodes, due to their large exciton binding energy (~60 meV). ZnO materials have potential spintronics because it is both theoretically predicted and experimental proven that ZnO-based diluted magnetic semiconductors can be ferromagnetic above room temperature. The process of "Sol-gel dip-coating" for film preparation is very attractive and cost-effective. Here the morphological structural and optical studies are taking place.

The structural studies of pure 0.5% Cobalt doped, 1.5% Cobalt doped ZnO thin films are taken. The XRD pattern of the thin film shows a dominating peak (002), indicating a high preferential x-axis-oriented wurtzite-type crystalline structure and polycrystalline with grains uniformly perpendicular to the surface substrate. The peaks occur at the range between 32°-37°. The energy band gap increases from 3.23 – 3.37 eV with increasing Co doping. The

morphological studies show that as the concentration of the dopant increases the intermolecular space decreases and the molecules become closer thus the conductivity increases and it also favours the ferromagnetic property of ZnO. It exhibits a hexagonal structure. The grain size increase as the doping concentration increases but all are at a nano scale. The optical studies show that the maximum range of absorbance occurs at the visible region. The absorbance increases as the dopant concentration increase. The obtained result proves that the ZnO pure and doped thin films elaborated by the sol-gel dip-coating technique can be used in wave-guiding and TCO for solar cells etc.

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