

HEXAGONAL WURTZITE MN DOPED ZnO NANOSTRUCTURED THIN FILM FOR FERROMAGNETIC AND LPG SENSING APPLICATIONS

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ABSTRACT: An economical environment friendly and easy to apply so called SILAR (successive ionic layer adsorption and reaction) method has been used to grow Mn doped ZnO nanostructured thin film over a glass substrate. The XRD-characterization reflects its Hexagonal wurtzite crystalline structure. The addition of deliberate amount of Mn concentration in to ZnO, increases the LPG sensing response of Mn doped ZnO compound deposited as nanostructured layer at lower temperatures. This compound also exhibit ferromagnetic behavior at room temperature with as determined saturated magnetization (M_s) at 601.21 E-6 emu/cm², which is in good agreement of BMPs model.

KEYWORDS: SILAR, XRD characterization, LPG sensing & response, ferromagnetism, BMPs model.

INTRODUCTION

A number of techniques have been explained to synthesize one dimensional zinc oxide nanostructures. Techniques like physical vapor deposition (1-3), chemical vapor deposition (4-6), molecular beam epitaxy (MBE) [7], pulsed laser deposition [8, 9], sputtering (10) and flux methods (11) etc. have been used earlier. In General here mentioned physical deposition techniques need more man-power and costly, requiring complicated instrumentation and vacuum system. On the other hand, wet chemical coating techniques are simple, eco-friendly and cost effective and thus have become the methods of choice. Amongst these techniques, Successive Ionic Layer Adsorption and Reaction is gaining popularity for its simplicity and environmental friendly procedure for obtaining stoichiometric Mn doped ZnO thin-film.

1. EXPERIMENTAL DETAIL

1.1 Synthesis

The ZnO thin film was deposited on glass substrate by SILAR technique. 0.015 M ZnSO₄ solution was prepared in 50mL distilled water which was considered as cationic precursor. Distilled water was considered as anionic precursor. Two to three drops of triethanolamine (TEA) was added to the ZnSO₄ Solution. pH was kept at 11 to 12 by adding ammonia. The glass slides were cleaned by labolene and then rinsed by distilled water and further by acetone. The glass slides were dipped in each precursor for 30sec, such 60 cycles were repeated and zinc oxide thin film was obtained. After preparing 0.015M MnSO₄ solution and putting the zinc oxide thin film for 1 min duration in it, desired Mn doped ZnO thin film was obtained.

2. RESULTS AND DISCUSSION

2.1 Characterization using X-ray diffraction analysis

Figure 1 indicates the X-Ray Diffraction pattern of as synthesized sample on the glass substrate. The X-Ray diffraction peaks observed close to $2\theta = 31.66, 34.6, 36.2$ and 47.0 are attributed to the (100), (002), (101) and (102) planes respectively which matches well with the JCPDS card No. 80-0075. The XRD pattern

reveals the good crystalline quality without any appreciable changes from pure zinc oxide films and is genuinely polycrystalline with a hexagonal wurtzite structure. These results proved that there are no secondary phases such as a manganese cluster or oxides and also there are no additional peaks seen due to Mn^{2+} ions substitution. But the Mn doped ZnO thin film grain size measured to be 26nm [11].

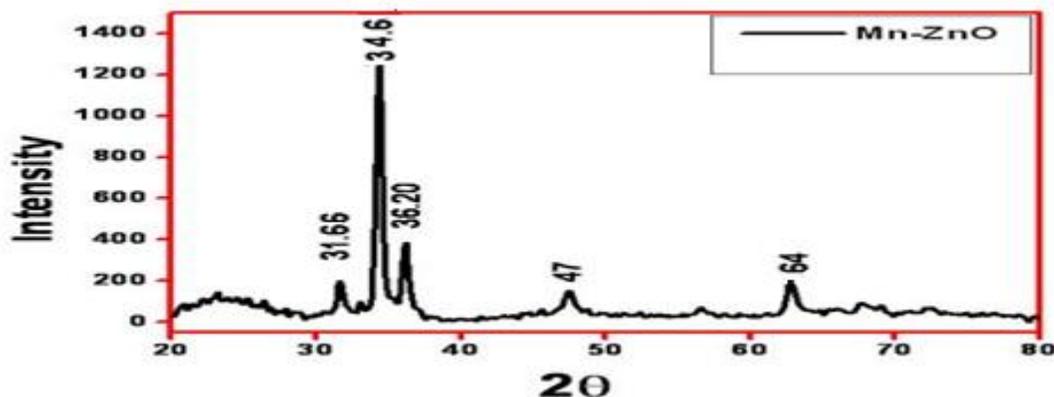


Fig.1: X-Ray Diffraction pattern of as grown Mn doped ZnO thin film.

2.2 LPG sensing Properties

Figure 2 implies the response curve of Mn doped ZnO thin film at operating temperature of (100-250 °C) as a function, in varying LPG atmosphere (200 ppm & 400 ppm). Proper substitution of Mn increases the crystallite size, decreases the grain boundary. Here, Mn works as viaduct in case of flow of electrons which may enhance the sensing property of Mn doped ZnO thin film. The fast response and recovery times (~8 sec and 10 sec respectively) were the main feature in this case. As the gas concentration enhanced the response was found to increase.

The LPG with changing concentrations (200 ppm and 400 ppm) was introduced successively into the analysis chamber. Initially with 200 ppm of LPG, the response was found to be almost 1.145 followed by excellent recovery on the removal of gas from the chamber. Later, with 400 ppm of LPG, the sample showed stable and reproducible response (1.17). The results were quite good than the earlier reports for LPG sensing with ZnO Thin films. [16, 17, 18].

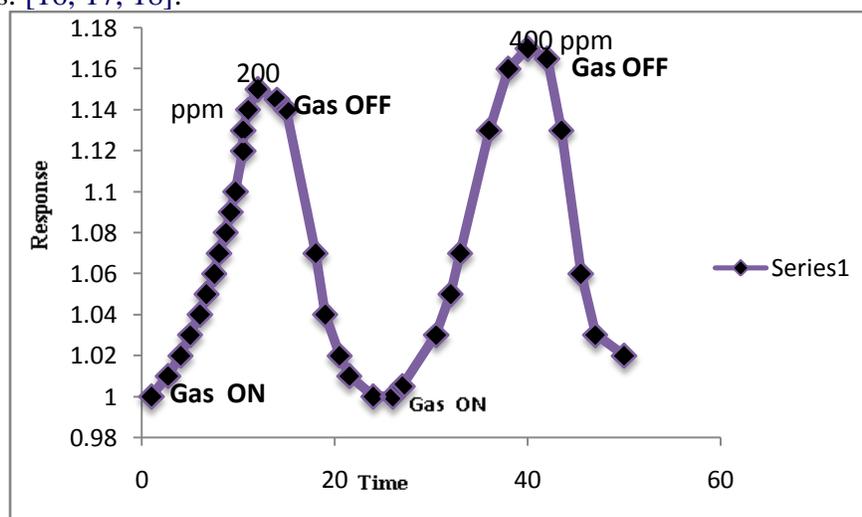


Fig.2: LPG sensing response of Mn -ZnO film

2.3 Magnetic properties of Mn doped ZnO thin films

The magnetization induced Vs field applied, M-H curve (Figure 2) for Mn doped ZnO thin film was plotted. The Mn doped ZnO thin film sample exhibit the characteristics of a ferromagnetic behavior magnetic field, and the saturated magnetization (M_s) is $601.21E-6$ emu/cm². The magnetic properties of dilute magnetic systems can be explained by bound magnetic polaron (BMP) model [12 & 13]. Considering the morphology of the Metal doped ZnO films which had Zn defects and Mn⁺ in the Mn doped ZnO film. The ferromagnetism observed in the film can be explained by using the BMPs model. The magnetic exchange interaction between ZnO and Mn⁺ occupying the same space is aligned with Mn¹⁺ spins, forming BMPs. According to this model an impurity site (donor or acceptor) plays the role of a trap and captures the carrier (electrons or holes) to form a bound polaron. These polaron are usually surrounded by the magnetic Mg ions. The polaron interaction with magnetic Mg ions causes the alignment fully or partially to generate the magnetic property of the system. Thus, the sample can exhibit ferromagnetism. Analogous behavior of room temperature Ferro-magnetism is exhibited by Mn doped ZnO thin films grown by SILAR.

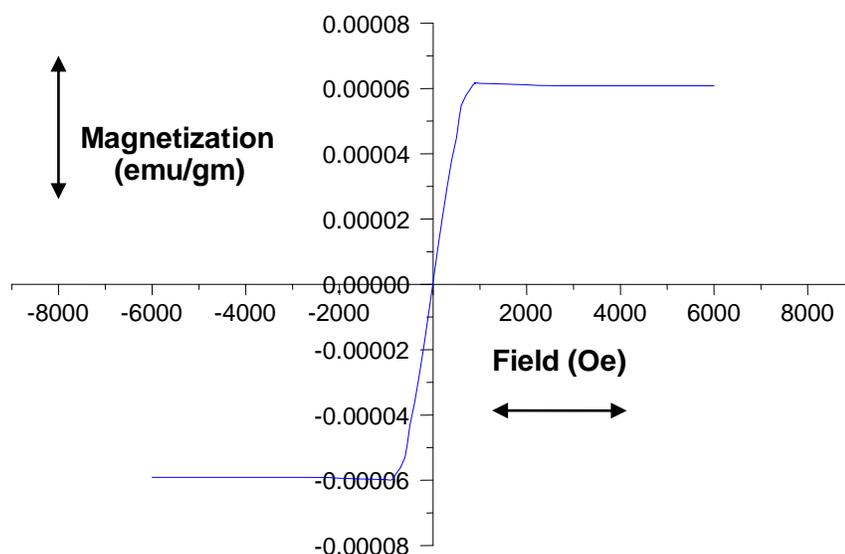


Fig.2: The magnetization, M-H curve, of as grown Mn-ZnO thin film.

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