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# FERROMAGNETISM IN THE (Zn,Mn)O THIN FILMS GROWN BY SPUTTERING RF AT HIGH OXYGEN PRESSURES

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**Abstract**

The electronic properties of semiconductor materials are extremely sensitive to impurities atomic, an example of this, are Diluted Magnetic Semiconductors (DMS) which are the most promissory materials in the spintronics new technology, which search to manipulate the intrinsic properties of the electron such as charge and spin. Theoretical calculations have established the probability of finding behaviour ferromagnetic in semiconductor types (II,VI) and (III,V) to doped with ions of magnetic elements such as Mn, Cd, among others. This has carries into an intense search for ferromagnetism at room temperature in these materials. We report in this work the study of the zinc oxide semiconductor doped with manganese Zn(Mn)O, in form of thin film grown by sputtering technique in a pure oxygen atmosphere. The results show that the wurtzite hexagonal structure of ZnO was conserved after the doped. However, is the presence of secondary phases $ZnMn_3O_4$ and $MnO_2$. The morphological characterization was carried out through an Atomic Force Microscope, finding that the average roughness decreases with the concentration of manganese of the matrix of zinc oxide. The curves showed a ferromagnetic transition at around 14 K. in thin films. Magnetic properties in these materials may be attributed to the double exchange interaction.

***Keywords:*** *Diluted Magnetic Semiconductors, Ferromagnetism, (Zn,Mn)O thin films.*

**Resumen**

Las propiedades electrónicas de materiales semiconductores son extremadamente sensibles a impurezas atómicas, un ejemplo de esto, son los Semiconductores Magnéticos Diluidos (SMD) los cuales son los materiales más promisorios en la nueva tecnología de espintronica, la cual busca manipular las propiedades intrínsecas del electrón tales como la carga y el espín. Cálculos teóricos han establecido la probabilidad de de encontrar un comportamiento ferromagnético en semiconductores del tipo (II,VI) y (III,V) al ser dopados con iones de elementos magnéticos tal como Mn, Cd entre otros. Esto ha llevado a una intensa búsqueda de ferromagnetismo a temperatura ambiente en estos materiales. En este articulo reportamos el estudio de oxido de zinc dopado con manganeso Zn(Mn)O, en forma de películas delgadas crecidas mediante la técnica de sputtering en un ambiente de oxigeno puro. Los resultados muestran que la estructura hexagonal tipo wurtzita del ZnO se conservo después del dopaje. Sin embargo, se halló la presencia de fases secundarias como $ZnMn_3O_4$ and $MnO_2$. La caracterización morfológica fue llevada por medio de un Microscopio de Fuerza Atómica, encontramos que la rugosidad media decrece con la concentración de manganeso de la matriz del oxido de zinc. Las curvas mostraron una transición ferromagnética alrededor de 14 K. en películas delgadas. Las propiedades magnéticas en estos materiales pueden ser atribuidas a la interacción de doble intercambio.

***Palabras claves:*** *Semiconductores Magnéticos Diluidos, Ferromagnetismo, Películas delgadas de (Zn,Mn)O*

## 1. INTRODUCTION

Semiconductor physics and magnetism fields a matter physics, conducting materials that combine semiconductor behaviour with a robust magnetism, has been a great dream for a long time in the physics of materials. A strategy for creating these systems is the introduction of localized magnetic moments in semiconductors, these are called Diluted Magnetic Semiconductors (DMS) [1]. DMS's are one of the most promising materials for

creating devices with new technology applications in spintronics, able to manipulate the properties of the electron such as charge and spin, moreover, theoretical calculations predict the probability of finding ferromagnetism at high temperatures for elements of the groups (II, VI) and (III, V) doped with magnetic ions as Mn or Cd, some DMS are GaAs and ZnO [2.3]. Many research aimed at the formation of thin films of DMS's have been developed using different techniques such as Molecular Beam Epitaxy - MBE, Pulsed Laser Deposition - PLD or RF-sputtering show divergent behaviour, while in some cases is reported ferromagnetism [4], other indicate paramagnetic states [5] or glass spin [6]. Magnetization observed are generally small $(< 0.15\mu_B / Mn)$ [7]. It seems that the magnetic moment decreases with increasing concentration of Mn, this implies the presence of ferromagnetic interactions [7.8].

Zinc oxide is a semiconductor type (II,VI) with gap a width of ~3.4 eV. It has a hexagonal structure, wurtzite type.

Dietl, establish the need for a 5% magnetic ions in the matrix of each semiconductor [3]. The limit of the solubility of manganese on the matrix of zinc oxide in conditions of thermal balance is approximately 13% [9], but this limit increases when using growth techniques outside of the thermodynamic balance. PLD solubility can be as high as 35% , while in MBE or sputtering becomes 20% [10].

In this paper, we report the magnetic properties in $Zn_{1-x}Mn_xO$ thin films grown by RF magnetron sputtering at high oxygen pressures, varying the Manganese concentration between 2 and 11% wt.

## 2. EXPERIMENTAL DETAILS

Target $Zn_{1-x}Mn_xO$ were stoichiometry home made, initially the powder were calcined at temperature of 673 K for 8 hours, after, using a pressure of 28 MPa for five minutes and the high temperature sintered process at 873 K for 13 hours and then 1173 K for 7 hours, according the reaction:

$$ZnO + MnO_2 \rightarrow Zn_{1-x}Mn_xO + O_2 \qquad (1)$$

for manganese concentrations of 2 and 11% wt. Structural characterization done by x-ray diffraction on targets shows that we obtained the wurzite-ZnO [11.12]. Thin films of $Zn_{1-x}Mn_xO$ were grown using the RF-magnetron sputtering technique, in an pure Oxygen atmosphere at a pressure of $7.0x10^{-3}$ mbar, with a net power of 80 W. Thin films were deposited on Si substrates at a substrate temperature of 623 K. Structural characterization on the thin films was performed by x-ray diffraction, the diffractometer used to measure the samples is a Philips Analytical X-ray B.V., type PW3710, with wavelength characteristic $K\alpha 1$, using a geometry $\theta$-$2\theta$, with a step of 0.02º. Magnetic characterization, magnetization as a function of temperature in the applied magnetic field of 300.0 Oe and magnetization as a function of field at constant temperature of 5 K, was conducted through a Physical Properties Measurement System, PPMS, of Quantum Design™.

Morphological characterization was carried out through an Atomic Force Microscope – AFM, with a SiN tip and constant elasticity of 10 $Nm^{-1}$. Scan area was 3x3 $\mu m^2$. Surface roughness values were statistically calculated through the SPIP V.4.2.4.0. program[12].

## 3. RESULTS AND DISCUSSION

X-ray diffraction pattern, not shown, showed that the films grew with Si substrate, wurtzite phase characteristic of the ZnO, as major phase; however there are contributions of $ZnMn_3O_4$ and $MnO_2$ secondary phases, as reported in previous work [12.13]. The pattern shows a privileged growth along (0 0 2). Figures 1 and 2 shows the magnetization curve as function of the temperature in the presence of a field of 300.0 for the samples $Zn_{0.98}Mn_{0.02}O$ and $Zn_{0.89}Mn_{0.11}O$. The curves indicates that there is a little ferromagnetism with a $T_c$ ~14 K in both cases, this critical temperature value has been calculated from remaining field in the magnetization curve (inset of figures 1 and 2 respectively) as function of the field, with H=0. Insets in fig. 1 and 2 shows the isothermic magnetizations as function of the field at a temperature of 5 K. The hysteresis curve show a weak ferromagnetic behavior, indicating that our samples grown by magnetron sputtering technique at pure oxygen pressure at a substrate temperature show a ferromagnetic behavior. The values of coercive fields extracted from the curve have a value of 62.1 Oe and 56.4 Oe respectively. The curves shown in figures 1 and 2 have been normalized to the values of saturation magnetization.

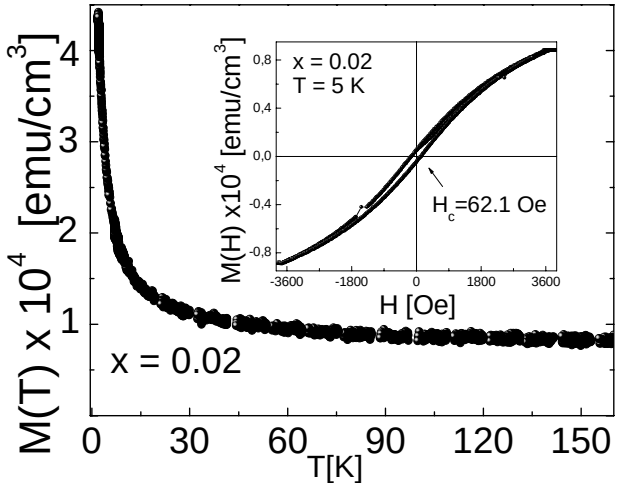



**Figure 1.** Magnetization as function of the temperature in a applied magnetic field of 300.0 Oe for the $Zn_{0.98}Mn_{0.02}O$ sample. The inset shows the magnetization curve as function of the field, in the -3000 TO +3000 Oe range, at a temperature of 5 K.

The interpretation of the origin of ferromagnetism in thin films of $Zn_{1-x}Mn_xO$ is controversial; however, we attribute the appearance of a small and not robust ferromagnetism due to the presence of new phases, in previous works, the appearance of secondary phases as $ZnMn_3O_4$ and $MnO_2$ in samples of $Zn_{0.89}Mn_{0.11}O$ are more evident than in samples of $Zn_{0.98}Mn_{0.02}O$[12.13]. The presence of new phases in the matrix of zinc oxide involve a little ferromagnetism [14].

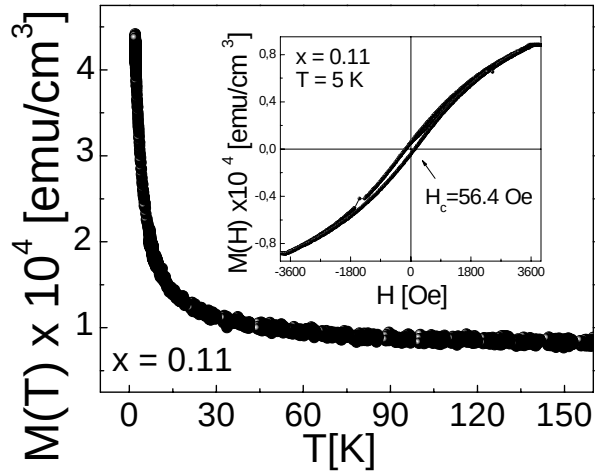



**Figure 1.** Magnetization as function of the temperature in a applied magnetic field of 300.0 Oe for the $Zn_{0.89}Mn_{0.11}O$ sample. The inset shows the magnetization curve as function of the field, in the -3000 to +3000 Oe range, at atemperature of 5 K.

Figure 3 shows an Atomic Force Microscopy surface image, for the sample $Zn_{0.89}Mn_{0.11.}$ The surface morphology with a roughness around 3.4 nm in a film thickness of around 350 nm estimate refinement through X-ray diffraction by method of Rietveld [12] indicates that our samples grew very flat, not dramatic changes in the surface images we found between the samples. Table 1 reflects the statistically values of roughness analyzed and calculated for each sample on which shows the decrease in roughness with the increase in the concentration of manganese [12].

**Table 1.** Roughness values of thin films system $Zn_{1-x}Mn_xO$ grown by sputtering RF.

| Samples | Roughness [nm] |
|---|---|
| $Zn_{0.98}Mn_{0.02}O$ | 3.4 ± 0.1 |
| $Zn_{0.98}Mn_{0.02}O$ | 2.1 ± 0.1 |

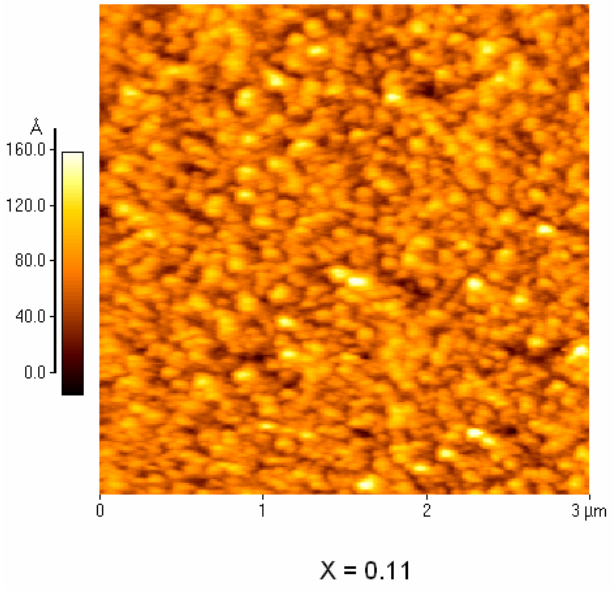



**Figure 3:** Image of atomic force microscopy of thin films of $Zn_{0.89}Mn_{0.11}O$.

## 4. SUMMARY AND CONCLUSION

The results shown that the samples of thin films of Diluted Magnetic Semiconductor system $Zn_{1-x}Mn_xO$ for Mn concentrations between 2 and 11% wt grown by magnetron sputtering technique at pure oxygen pressure at a substrate temperature show a ferromagnetic behavior.

The system $Zn_{1-x}Mn_xO$, the surface morphology depends on the parameters of growth rather than the concentration of manganese in the matrix of zinc oxide, however, there is a decrease of the roughness with increased concentrations of manganese.

During the growth of thin films of DMS $Zn_{1-x}Mn_xO$, high temperatures in substrate deposition cathodic generate secondary phases $ZnMn_3O_4$ and $MnO_2$ in the matrix of zinc oxide.

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