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IMPACT OF SULFUR CONCENTRATION ON THE MAGNETIC AND ELECTRICAL CHARACTERISTICS OF ZnMnO THIN FILMS

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Influence of the sulfur doping on the structural, optical, electrical and magnetic properties of ZnMnO thin films fabricated using the ultrasonic spray pyrolysis technique was investigated. Our study reveals that increasing sulfur content leads to a noticeable shift in the band gap energy towards the red spectrum, an indicator of altered electronic states and potential for enhanced spintronic functionalities. The strong reduction in the band gap for the sulfur doped ZnMnO alloys is the result of the upward shift of the valence-band edge. As a result, the room temperature bandgap of $ZnMnO_{1-x}S_x$ alloys can be tuned from 3.2 eV to 2.97 eV for $x \leq 0.2$. The observed large bowing in the composition dependence of the energy bandgap arises from the anticrossing interactions between the valence-band of ZnO and the localized sulfur level above the ZnMnO valence-band maximum. The doping process significantly modifies the ferromagnetic properties, with an observed increase in Curie temperature correlating with higher sulfur concentrations. These changes are attributed to the increased free holes concentration, which facilitates a more robust exchange interaction between the magnetic ions. Additionally, the structural assessments via scanning electron microscopy confirm the uniform integration of sulfur into the ZnMnO matrix, resulting in distinct nanocrystalline formations. This study contributes to the understanding of doping mechanisms in semiconductor materials, especially for highly mismatched alloys, where the anions are partially substituted with isovalent atoms of considerably different size and/or electronegativity, offering insights into the tunability of their magnetic and electronic properties for potential future applications in spintronic devices.

Keywords: *Diluted magnetic semiconductors; Mn-doped p-type ZnO; Isovalent anion alloying; ZnO-ZnS alloy; Sulfur-doped ZnMnO; Resistivity anomaly; Valence band (VB) offset bowing; Defined hysteresis loop; Critical point; Curie temperature*
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INTRODUCTION

Diluted magnetic semiconductors (DMSs) have attracted increasing attention in last 20 years [1]. The exchange effect between magnetic ions and carriers in semiconductors gives DMSs novel magneto-electric and magneto-optical properties. In addition, DMSs take advantage of both the charge and spin properties of electrons, making them potentially widely useful in spin field effect transistors (spin-FETs), high-density nonvolatile memory and spin qubits for quantum computers [2]. There are two main factors that limit the practical application of DMSs in equipment. The first is that the Curie temperature of DMS material is lower than room temperature, and the second is whether the ferromagnetism in DMS material is intrinsic, that is, mediated by free carriers, or purely from the local secondary phase of magnetic dopants, such as clusters or precipitates. If ferromagnetism is not mediated by free carriers, spin polarization cannot be carried by them.

In the seminal paper by T. Dietl et al. [3] it was theoretically predicted a room temperature ferromagnetism (RTFM) in at 5% Mn-doped *p*-type GaN and ZnO, with free holes concentration about $10^{20} cm^{-3}$. ZnO suffer from a low concentration of free holes and isovalent anion alloying can improve this problem. ZnO and ZnS alloy exhibits a very strong valence band (VB) offset bowing as a function of sulfur content [4]. The VB-bowing can be utilized to enhance *p*-type doping with lower formation energy and shallower acceptor state in the ZnO-ZnS alloy.

In this work, structural, optical and magnetic properties of $Zn_{1-x}Mn_xO_{1-y}S_y$, additionally doped with nitrogen, thin films grown by ultrasonic spray pyrolysis system are reported.

EXPERIMENTAL PART

Sulfur-doped ZnMnO thin films were deposited on Si [100] substrates using the ultrasonic spray pyrolysis method (USP). Aqueous chemicals were utilized during the solution preparation. Zinc acetate dihydrate ($Zn(C_2H_3O_2)_2\ 2H_2O$) and manganese acetate tetrahydrate ($Mn(C_2H_3O_2)_2\ 4H_2O$) were used as sources of zinc and manganese, respectively. Thiourea ($SC(NH_2)_2$) and ammonium acetate ($C_2H_7NO_2$) were added in appropriate quantities for the sulfur and nitrogen doping. The substrate was cleaned for 10 *min* in hydrofluoric acid, acetone, ethanol and D.I. water to remove impurities and organic solvents. Molar ratio of zinc acetate dihydrate was 0.3 *mol*/*l* while manganese concentration was kept same 5% of Zn for all samples. We employed an ultrasonic nebulizer with 2.4 M*Hz* frequency for atomizing prepared solution. The substrate temperature was set 400 ºC while growing thin film. All samples were annealed after grows at 500⁰C for 15 minutes. Thickness of the samples was approximately 500 *nm*.

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The morphology was studied with the scanning electron microscope (SEM). The crystallographic properties of the films were analyzed by Rigaku Miniflex X-ray diffractometer (XRD) using the CuKa radiation. The optical properties of the films were measured with a UV/VIS spectrometer. The magnetic properties were measured by using the superconducting quantum interference device (SQUID) magnetometer (Quantum design MP MS XL).

RESULTS AND DISCUSSION

Figure 1 shows SEM images (a) top and (b) side views of hexagonal-shaped nanocrystals, whose sizes were estimated between 150-200 *nm*. From the side view, thickness of sample could be seen around 500 *nm*.

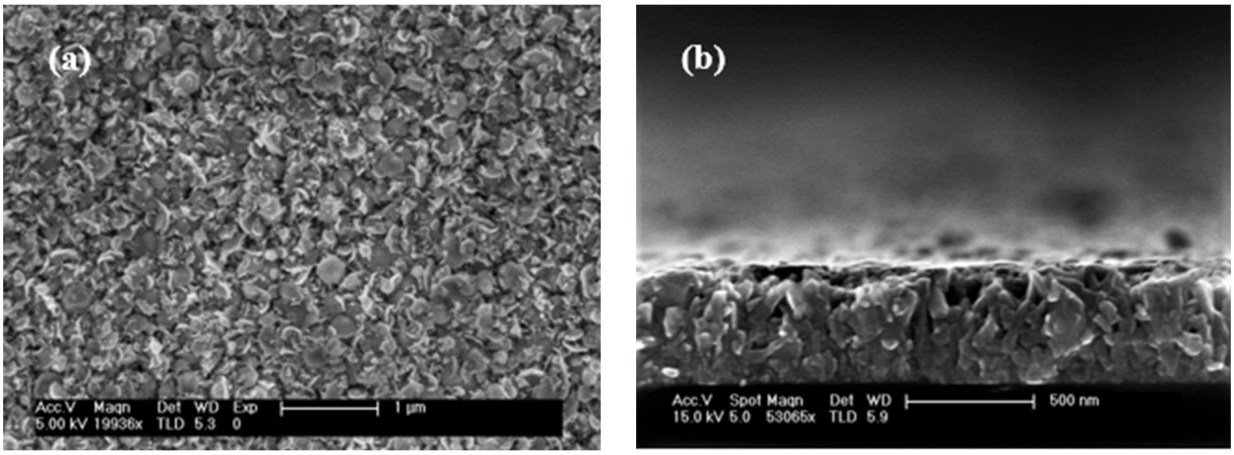

Figure 1. SEM images (a) top and (b) side views of the nitrogen doped $Zn_{0.95}Mn_{0.05}O_{0.90}S_{0.1}$ thin film

Figure 2 shows the XRD patterns for the pure ZnO and the $Zn_{1-x}Mn_xO_{1-y}S_y$, with 5% of Mn and different concentrations of S thin films grown on a silicon substrate by using the USP method. A dominant diffraction peak for (002) indicates a high degree of orientation with the *c*-axis vertical to the substrate surface. The shift of the (002) diffraction peak to the lower angle demonstrates a successful incorporation of the sulfur into ZnO lattice since the lattice constant $c = 6.26$ Å for ZnS is larger than 5.21 Å for ZnO [5]. It is also seen from Fig. 2, that the (002) peak is widening with increasing of the sulfur concentration which is due to the decreasing of the average size of crystal grains and the alloying effect. The diffraction peaks shown in Fig. 2 by star symbol demonstrate the existence of the Mn_2O_3 precipitates, even so the concentration of Mn in the samples was limited to the 5 %.

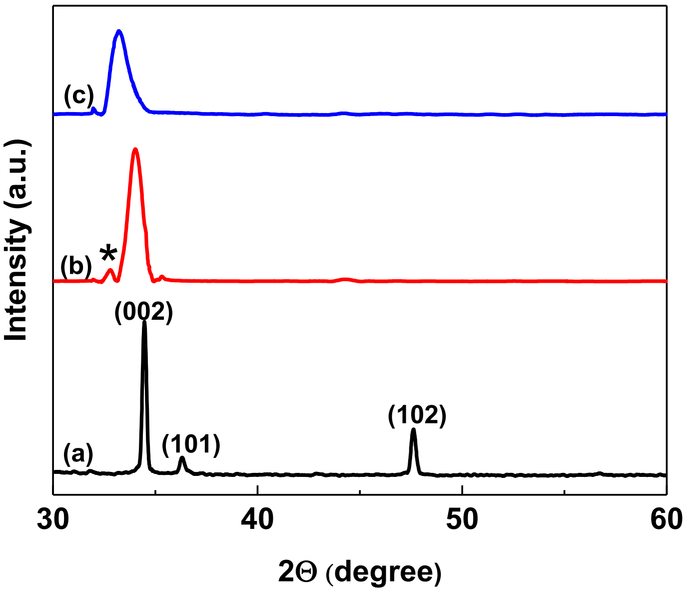

Figure 2. X-ray diffraction spectra of a) pure ZnO, b) $Zn_{0.95}Mn_{0.05}O_{0.9}S_{0.1}$, and c) $Zn_{0.95}Mn_{0.05}O_{0.80}S_{0.20}$ thin films, respectively. The diffraction peak of Mn_2O_3 shown by star symbol

The band gap energy of ZnMnO, 10% and 20% sulfur doped ZnMnOS can be determined from the Tauc plot ($\alpha h\nu = A(h\nu - E_g)^{1/2}$) equation [6]. Figure 3 shows $(\alpha h\nu)^2$ vs. phonon energy and each extrapolation represent the band gap energy of the thin film grown on Si substrates. Results show successfully incorporation of sulfur into ZnMnO films.

Band gap energy is decreasing with sulfur concentration increasing. The $Zn_{0.95}Mn_{0.05}O_{0.8}S_{0.2}$ sample has the band gap of 2.97 *eV*, while $Zn_{0.95}Mn_{0.05}O$ thin film remains almost 3.2 *eV* as same as pure zinc oxide. So, overall red shift was observed in band gap energy. This directly reduced activation energy of the nitrogen acceptors. And, the Hall measurements show 5.1×10^{16} cm^{-3} and 4.85×10^{17} cm^{-3} of the free holes' concentrations in 10% and 20% of sulfur doped samples, respectively. $ZnO_{1-x}S_x$ alloys are classified as highly mismatched alloys (HMAs), semiconductor compounds where the anions are partially substituted with isovalent atoms of considerably different size and/or electronegativity.

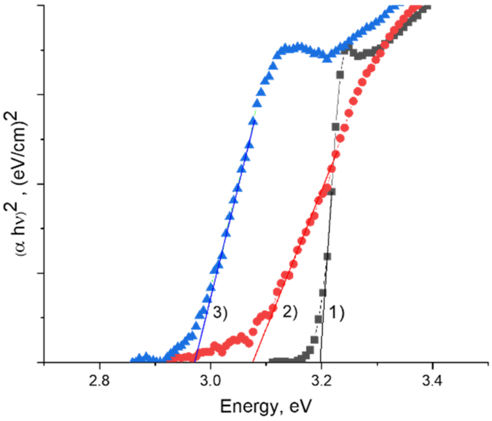

Figure 3. Tauc plots of the $Zn_{0.95}Mn_{0.05}O_{1-x}S_xN$ for 1) 0%, 2) 10% and 20 % of the sulfur concentrations, respectively.

Due to the high mismatch, the bandgap of these materials cannot be easily predicted with the virtual crystal approximation (VCA) model or modified VCA models [7]. The bandgap of HMA drastically decreases by the substitution of a small fraction (few percent) of anions with an isovalent element. The electronic band structure of HMAs is well described by the band anticrossing (BAC) model that considers an interaction between localized states introduced by the minority anions and the extended states of the host conduction/valence band in the dilute alloy composition limit [7].

Applying external magnetic field to the 10% and 20% sulfur doped samples at 10 K shows well-defined hysteresis loop for both samples (Fig. 4). Results represent both sample are ferromagnetic at 10 K. The magnetization completely saturated at ±1000 Oe (Oersted). It is obvious that sulfur is not a magnetic element, but 20% sulfur doped sample represent higher saturation magnetization value than that of 10% sulfur doped thin film. This could be explained by increase in the concentration of free holes. Because, the exchange interaction between magnetic ions is mediated by free holes, which are increased by adding more sulfur into ZnMnON thin film.

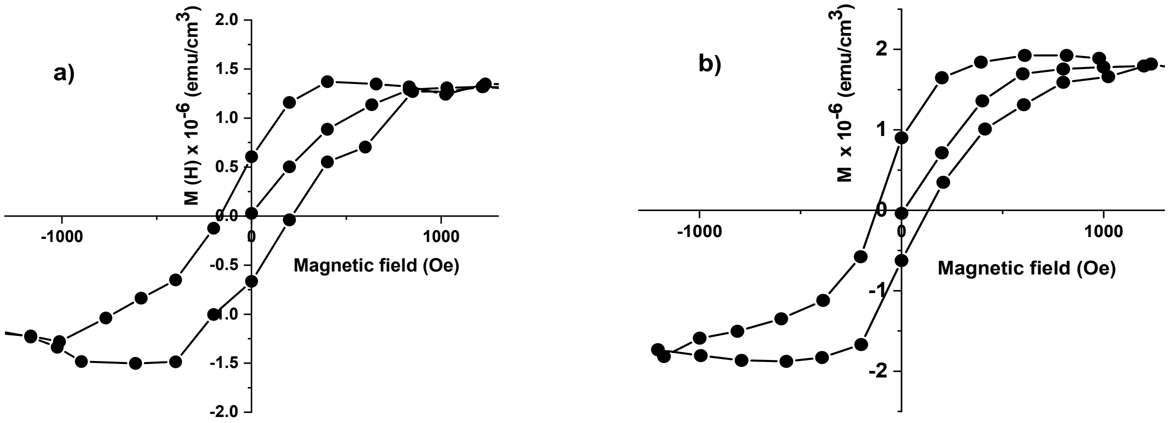

Figure 4. Magnetic field dependence of the magnetization (Hysteresis loop) at 10 K for
a) $Zn_{0.95}Mn_{0.05}O_{0.9}S_{0.1}$ and b) $Zn_{0.95}Mn_{0.05}O_{0.8}S_{0.2}$ thin films.

Figure 5 shows the magnetization dependence on temperature for a) $Zn_{0.95}Mn_{0.05}O_{0.9}S_{0.1}$ and b) $Zn_{0.95}Mn_{0.05}O_{0.8}S_{0.2}$ thin films in the temperature range from 10 K to 300 K. Results show that the value of magnetization for the $Zn_{0.95}Mn_{0.05}O_{0.9}S_{0.1}$ and $Zn_{0.95}Mn_{0.05}O_{0.8}S_{0.2}$ samples is higher than zero until temperature reached 170 K and 200 K, respectively. These measurements demonstrate the increasing the sulfur concentration in ZnMnO causes some increase in the Curie temperature. In the low temperature region < 50 K, the magnetization value is significantly high.

This could be explained by existing of the manganese oxide precipitates. Because of the low growing temperature, Mn_3O_4 ferromagnetic phase of the manganese oxide was formed, with Curie temperature near 47 K [8]. So that reason, the magnetization value enhances below 50 K.

In the ferromagnetic state (below T_C), the spins of magnetic ions become aligned, resulting in less scattering of the spin polarized charge carriers and low resistivity. As the temperature approaches the critical point, the most disordered state of spins is formed. For ferromagnets with a small concentration of free carriers the T_C is attributed to the maximum of resistivity as it follows from the theory of the resistivity anomaly at T_C in ferromagnets given by de Gennes and Fridel [9].

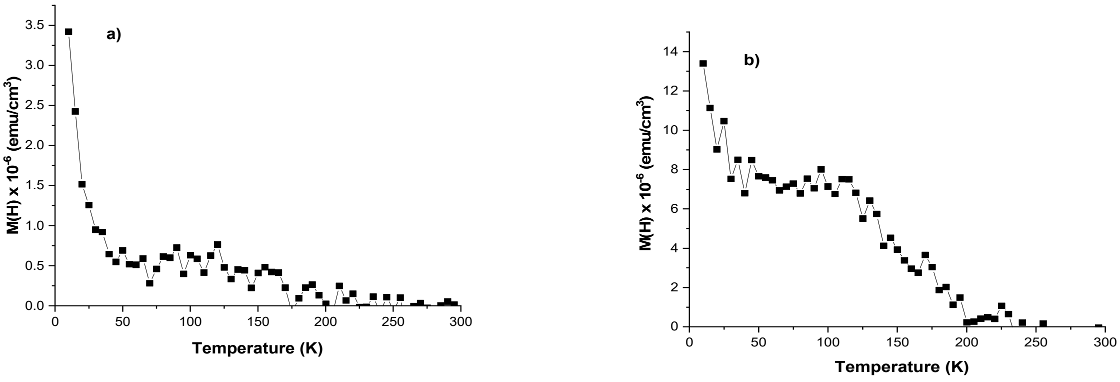

Figure 5. Magnetization dependence on temperature
a) $Zn_{0.95}Mn_{0.05}O_{0.9}S_{0.1}$ and b) $Zn_{0.95}Mn_{0.05}O_{0.8}S_{0.2}$ thin films in temperature range from 10 K to 300 K

Figure 6 shows the resistivity peaks near 170 K and 200 K for 10% and 20% sulfur-doped ZnMnO, respectively.

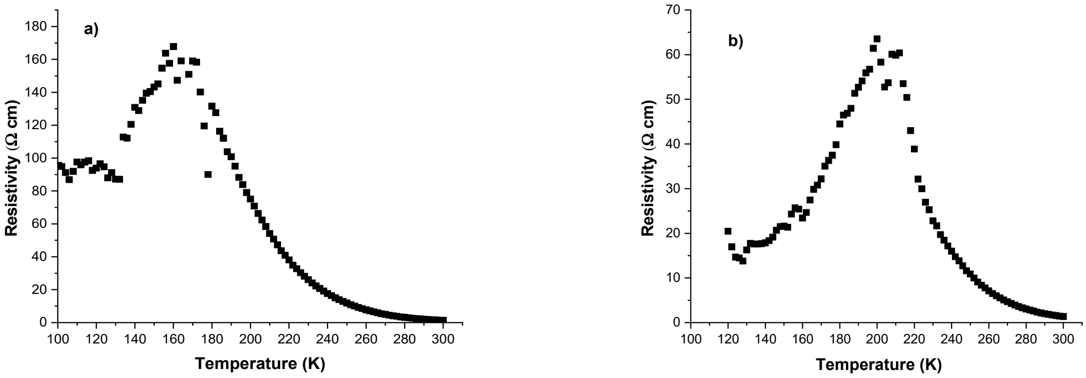

Figure 6. Temperature dependence of the resistivity
a) $Zn_{0.95}Mn_{0.05}O_{0.9}S_{0.1}$ and b) $Zn_{0.95}Mn_{0.05}O_{0.8}S_{0.2}$ thin films, respectively

From these results the ferromagnetic to paramagnetic phase transition can be observed, and the Curie temperature also can be determined by finding the highest resistivity point. These critical temperatures values determined from the resistivity peaks coincide well with critical temperatures found by the magnetization measurements presented above in Fig.4. When temperature is higher than T_C, resistivity decreases again as the material loses its magnetic ordering.

CONCLUSIONS

This study systematically explores the impact of sulfur doping on the properties of ZnMnO thin films, synthesized using ultrasonic spray pyrolysis. Our findings confirm that sulfur doping effectively shifts the band gap energy towards the longer wavelengths, thereby enhancing the magnetic properties of the films. We observed a notable increase in Curie temperature as the sulfur concentration increased. The enhanced hole concentrations facilitate stronger exchange interactions between magnetic ions.

The Curie temperature was determined for both 10% and 20% sulfur-doped ZnMnON by magnetization measurements, with hysteresis loops observed at 10 K. Near the Curie temperature, resistivity peaks were observed. The critical point, marking the ferromagnetic to paramagnetic phase transition temperature, was determined from the resistivity peak.

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REFERENCES

[1] H. Kalita, M. Bhushan, and L.R. Singh, Materials Science and Engineering: B, **288**, 116201 (2023). https://doi.org/10.1016/j.mseb.2022.116201

[2] S.J. Pearton, C.R. Abernathy, M.E. Overberg, G.T. Thaler, D.P. Norton, N. Theodoropoulou, A.F. Hebard, *et al.*, Journal of Applied Physics, **93**, 1 (2003). https://doi.org/10/1063/1.1517164

[3] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science, **287**, 1019 (2000). https://doi.org/10.1126/science.287.5455.10
[4] C. Persson, C. Platzer-Björkman, J. Malmström, T. Törndahl, and M. Edoff, Phys. Rev. Lett. **97**, 146403 (2006). https://doi.org/10.1103/PhysRevLett.97.146403
[5] O. Madelung, *Semiconductor basic data,* (Springer-Verlag, Berlin, 1996).
[6] J. Tauc, Materials Research Bulletin, **3**, 37 (1968). https://doi.org/ 10.1016/0025-5408(68)90023-8
[7] J. Wu, W. Shan, and W. Walukiewicz, Semiconductor Science and Technology, **17**, 860 (2002). https://doi.org 10.1088/0268-1242/17/8/315
[8] L.W. Guo, *et al*., Journal of Magnetism and Magnetic materials, **123**, 321 (2000). https://doi.org/10.1016/S0304-8853(00)00008-1
[9] P.G. de Gennes, and J. Friedel, J. Phys. Chem. Solids, **4**, (1958). https://doi.org/10.1016/0022-3697(58)90196-3

ВПЛИВ КОНЦЕНТРАЦІЇ СІРКИ НА МАГНІТНІ ТА ЕЛЕКТРИЧНІ ХАРАКТЕРИСТИКИ ТОНКІХ ПЛІВОК ZnMnO

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Досліджено вплив легування сіркою на структурні, оптичні, електричні та магнітні властивості тонких плівок ZnMnO, виготовлених методом ультразвукового розпилювального піролізу. Наше дослідження показує, що збільшення вмісту сірки призводить до помітного зміщення енергії забороненої зони в бік червоного спектру, індикатора змінених електронних станів і потенціалу для покращених функцій спінтроніки. Сильне зменшення забороненої зони для легованих сіркою сплавів ZnMnO є результатом зсуву вгору краю валентної зони. У результаті ширина забороненої зони при кімнатній температурі сплавів $ZnMnO_{1-x}S_x$ може бути налаштована від 3,2 еВ до 2,97 еВ для $x \leq 0{,}2$. Спостережуване велике викривлення в залежності від складу забороненої зони виникає через антикросингові взаємодії між валентною зоною ZnO та локалізованим рівнем сірки вище максимуму валентної зони ZnMnO. Процес легування суттєво змінює феромагнітні властивості, спостерігаючи підвищення температури Кюрі, що корелює з вищими концентраціями сірки. Ці зміни пояснюються збільшенням концентрації вільних дірок, що сприяє більш міцній обмінній взаємодії між магнітними іонами. Крім того, структурні оцінки за допомогою скануючої електронної мікроскопії підтверджують рівномірну інтеграцію сірки в матрицю ZnMnO, що призводить до чітких нанокристалічних утворень. Це дослідження сприяє розумінню механізмів допування в напівпровідникових матеріалах, особливо для сплавів із сильною неузгодженістю, де аніони частково заміщені ізовалентними атомами значно різного розміру та/або електронегативності, пропонуючи розуміння регулюваності їхніх магнітних та електронних властивостей для потенціалу. майбутні застосування в спінтронних пристроях.

Ключові слова: *розчинені магнітні напівпровідники; Mn-легований ZnO p-типу; легування ізовалентним аніоном; сплав ZnO-ZnS; легований сіркою ZnMnO; аномалія питомого опору; зсув валентної зони (VB); визначена петля гістерезису; критична точка; температура Кюрі*