ZnO:Mn nanorods and ZnO/ZnO:Mn core/shell structures: Synthesis and local atomic structure.

O.E. Polozhentsev¹, V.L. Mazalova¹, V.E. Kaidashev¹, E.M. Kaidashev¹, Ya. Zubavichus², A.V. Soldatov¹

¹ Southern Federal University, Rostov-on-Don, Russia
² Kurchatov center of synchrotron radiation and nanotechnology, Moscow

E-mail: olegpolozhentsev@mail.ru

Abstract. Investigation on local atomic structure of ZnO:Mn nanorods, thin films and nanoscale core/shell structures ZnO nanorods/ZnO:Mn film (10% Mn concentration) has been performed. The structures are synthesized with high pressure pulsed-laser deposition (PLD) method. Synthesis and growth of the studied structures have been considered in detail for the determination of Mn embeddings and impurities in ZnO host lattice. Theoretical analysis of experimental data have been carried out using a self-consistent real space multiple scattering method (FEFF8.4 code) and a finite difference method (FDMNES2008 code). Local structure parameters have been refined using multidimensional interpolation approach on the basis of fitting XANES spectra (Fitit2.0 code). The samples synthesized under certain condition may contain both Mn embeddings and secondary phases. It is found that the most probable model of the Mn embeddings is the structure where Mn atoms substitute for Zn atoms but a part of Mn atoms is located in interstitial sites in ZnO host lattice.

1. Introduction
Investigation of diluted magnetic semiconductors has drawn considerable attention due to their further applications in a new generation of electronic and optoelectronic devices. Creation of nanoscale structures, including semiconductor micro- and nanorods and core/shell structures, possessing both good light emitting abilities and magnetic properties is especially actual. Zinc oxide is a widegap semiconductor material, perspective for creation of such devices and due to good mechanical characteristics is also a perspective material for creation of diluted magnetic semiconductors that are the semiconductors doped by magnetic transition metal (TM) ions in small concentration. Theoretical results predict that TM ions embeddings in small concentration in ZnO host lattice should promote an appearance of a ferromagnetic phase without additional doping, but experimental results remain controversial. Many reports on the observation ferromagnetism (FM) at a room temperature in transition-metal-doped ZnO have made this widegap semiconductor still more attractive to applications in spintronics and nanophotonics [1,2].

In the present work the analysis of x-ray absorption near edge structure (XANES) of the ZnO:Mn diluted magnetic semiconductors has been applied to study peculiarities of a synthesis process and local atomic structure of ZnO:Mn nanorods and ZnO/ZnO:Mn core/shell structures.
2. Experiment and methods of calculation.
Investigation of pure ZnO, Mn doped ZnO nanorods and ZnO/ZnO:Mn core/shell structures (ZnO nanorods/ZnO:Mn film) has been performed.

ZnO:Mn nanorods on α-plane sapphire have been synthesized by high pressure pulsed laser deposition (PLD) method under Ar pressure with the use of a thin film of Au catalyst. The characteristic sizes of the nanorods are about 50 nm in diameter and 1 μm along.

ZnO/ZnO:Mn core/shell structures have been synthesized in two step with the use of high pressure pulsed laser deposition method: ZnO nanorods under Ar pressure with the subsequent growth of a film on the surface of nanorods under oxygen pressure. Core/shell structures were synthesized from the targets sintered at 1150°C (the sample #1) and 550°C (the sample #2) temperatures at a 35 mm target-to-substrate distance. The nanorods and core/shell structures have been growth at 850°C. The concentration of Mn atoms in ZnO films and nanorods is about 10%. The studied materials were synthesized at the Laboratory of Nanotechnology, SFU, Rostov-on-Don, Russia[3,4].

Experimental Zn K-edge XANES spectrum of ZnO nanorods and Mn K-edge XANES spectra of ZnO:Mn nanorods and ZnO/ZnO:Mn core/shell structures have been measured in fluorescence mode using a NaI(Tl) scintillator detector with a photoelectronic multiplier at the synchrotron radiation facility “SIBERIA-2” (Kurchatov Center of Synchrotron Radiation and Nanotechnology, Moscow).[5]

Experimental Mn K-edge XANES spectra of Mn oxides(II,III,IV) have been measured in transmission mode using a crystal monochromator Ge(311) and a SC-70 detector at «Rigaku» R-XASLooper Spectrometer, Research Center for Nanoscale Structure of Matter, Southern Federal University, Rostov-on-Don, Russia.

Theoretical analysis of experimental XANES data have been carried out using ab initio self-consistent full multiple scattering calculations realized in FEFF8.4 code[6] and full potential finite difference method implemented in FDMNES2008 code[7].

Local structure parameters have been refined using Fitit2.0 code [8]. Principal Component Analysis (PCA) (realized in Fitit2.0 code) have been used to determine the concentrations of different secondary phase in the studied compounds.

3. Results and discussions
For the determination of Mn embeddings and impurities in ZnO host lattice we studied the synthesis and growth process under the different conditions. Figure 1 shows the experimental Mn K-XANES spectra for core/shell structures, together with ones of Mn oxides (II,III,IV) as references. It is found that under certain synthesis conditions of core/shell structures, various types of film structure on a nanorods surface are formed. Core/shell structures synthesized with the target sintered at 550°C are deposited with a formation of impurities corresponding to Mn oxide (III) that does not occur for

![Figure 1](image-url)
condition at 1150°C. Percentage of various secondary phases in the core/shell structures was
determined with PCA method. For the sample #2, the percentage of manganese oxide (III) is more than
90%. For the sample #1 we can conclude that Mn oxidation state for the sample #1 is lower than one
for the sample #2.

Theoretical analysis of XANES spectra above Zn and Mn K-edge has been performed and
theoretical methods have been tested with the well-known structure of bulk Zn oxide. Investigation of
the influence of the muffin-tin approximation on the shape of the theoretical spectrum has been
performed. Figure 2 shows the comparison between the experimental Zn K-edge spectra for ZnO and
theoretical spectra calculated with the use of muffin-tin (MT) approximation and in so-called ‘full
potential’ (beyond MT model), realized in FDMNES2008 code.

As one can see in figure 2 the theoretical spectra are in a good agreement with the experimental Zn
K-edge spectrum of ZnO bulk and the influence of the MT approximation on the shape of the
theoretical spectra is not essential, therefore we can apply these two approaches for calculations
XANES spectra for ZnO:Mn structures. Both approaches have been applied to simulate Zn and Mn K-
XANES spectra in ZnO bulk and Mn oxides. In figure 3 we compare the experimental Zn K-XANES
spectrum of ZnO bulk(curve 1) and the theoretical spectra calculated using FEFF8.4 (curve 2) and
FDMNES2008 (curve 3) codes. The best agreement with experimental Zn K-XANES spectra has been
reached using FDMNES2008 code. Therefore all calculations for ZnO:Mn structures were performed
with the use of FDMNES2008 code.

Different positions of Mn ions distribution for ZnO:Mn structures (such as vacancy, Zn and O
substitutional atom, interstitial atom, Mn clusters, and secondary phase) in the ZnO host lattice have
been examined. Figure 4 shows the comparison of the experimental Mn K-XANES spectra of
nanorods (curve 1) and core/shell structures (curves 2,3) with the theoretical spectra (curves 4,5,6)
calculated for several defect models such as Zn substitutional atoms, interstitial atoms, Zn
substitutional and interstitial atoms, Mn clusters and secondary phases in the ZnO host lattice.
Comparing the experimental Mn K-XANES spectrum for the ZnO:Mn(10%) nanorods and the
experimental spectrum for the sample #1 (figure 4), one can conclude that the sample #1 and nanorods
were synthesized under the same conditions. The theoretical XANES spectra for the models Zn
substitutional atoms (curve 4) and Zn substitutional and interstitial atoms well agree with the
experimental one in the intensity and the energy position of A1, A2, B, C, D, E features. Theoretical
spectrum for interstitial atoms disagrees with the experimental one.
It is found that the most probable model of the Mn embeddings is the structure where Mn atoms substitute for Zn atoms but a part of Mn atoms is located in interstitial sites in ZnO host lattice.

4. Conclusions
Investigation of pure ZnO and Mn doped ZnO nanorods and ZnO/ZnO:Mn core/shell structures (ZnO nanorods/ZnO:Mn film) has been performed. ZnO:Mn structures have been synthesized under various conditions by high pressure pulsed laser deposition (PLD) method. It is found that under certain conditions of the synthesis of core/shell structures, various types of structure of a film such as Mn embeddings, secondary phases on a surface of nanorods are formed.

Theoretical analysis of XANES experimental spectra above Mn K-edge has been performed. The most probable model of the Mn embeddings is the structure where Mn atoms substitute for Zn atoms but a part of Mn atoms is located in interstitial sites in ZnO host lattice.

Acknowledgements
The research is supported by grants of RFBR (Russia)-Academy of Science (Romania) 07-02-9187 and Ministry of Education and Science (Russia) 2.1.1.5932.

References
[1] Qinghua Liu, Wensheng Yan, He Wei, Zhihu Sun, Zhiyun Pan, A.V. Soldatov, Cong Mai, Congjian Pei, Xinfeng Zhang, Yong Jiang, and Shiqiang Wei. Phys. Rev. B 77, 245211 (2008).
[2] Zhihu Sun, Wensheng Yan, Guobin Zhang, Hiroyuki Oyanagi, Ziyu Wu, Qinghua Liu, Wening Wu, Tongfei Shi, Zhiyun Pan, Pengshou Xu, and Shiqiang Wei. Phys. Rev. B 77, 245208 (2008).
[3] Th. Nobis, E.M. Kaidashev, A. Rahm, M. Lorenz, and M. Grundmann, Phys. Rev. Lett. 93, No 10, 103903 (2004).
[4] M. Lorenz, E.M. Kaidashev, A. Rahm, Th. Nobis, J. Lenzner, G. Wagner, D. Spemann, H. Hochmuth, and M. Grundmann, Appl. Phys. Lett. 86, 143113 (2005).
[5] Chernyshov A A, Veligzhanin A A, Zubavichus Y V, Nucl. Instr. and Meth. A 603 (2009) P.95
[6] Rehr J J and Ankudinov A L 2005 Coord. Chem.Rev. 249 131
[7] Joly Y 2001 Phys. Rev. B 63 125120
[8] Smolentsev G., Soldatov A., J. Synchrotron Radiation 2006, 13, 19-29.