

Effect of Mn-doping Concentration on the Structural & Magnetic Properties of Sol-Gel Deposited ZnO Diluted Magnetic Semiconductor

Saira Riaz, Mehwish Bashir, Syed S. Hussain and Shahzad Naseem

Centre of Excellence in Solid State Physics, University of the Punjab, Lahore-54590, Pakistan

saira_cssp@yahoo.com

Abstract - Dilute Magnetic Semiconductors (DMS) are gaining interest at a very fast pace due to the possibility of their integration with the current semiconductor technology. This research includes preparation and characterization of Mn doped ZnO thin films. Films are prepared through Sol - Gel spinning method. The Sol - Gel technique used is the standard one in which solutions are mixed and spun onto the glass substrate. Different samples of $Zn_{1-x}Mn_xO$ are prepared where x varies from 0 to 0.25. Composition of all the samples is measured by using ICP spectrometer. XRD is used to study all the films structurally. XRD results show polycrystalline nature of all Mn-doped ZnO thin films. Increment in full width at half maximum (FWHM) is observed by increasing the Mn content in ZnO films indicating smaller grain size of thin films. SEM results are also in agreement with the XRD patterns. Nano-rods with diameter ~100 nm in Mn:ZnO thin films were observed. Mn:ZnO nano-tweezers have been observed for the first time with the feature size as low as 25nm. Magnetic properties are measured using VSM at room temperature. Higher magnetization values and lower shape anisotropy is observed.

Index Terms - Sol-gel, ZnO, Mn, Diluted magnetic semiconductor

1. Introduction

Doping of magnetic impurities in small amount into the semiconductor host lattices result in an outstanding class of materials known as diluted magnetic semiconductors (DMSs)¹. DMSs are extensively used in spintronics (spin + electronics) devices, magneto-optical switching, spin valve transistors, spin polarized lasers, spin light emitting diodes, non-volatile memory and magnetic recording due to their ability to control spin and charge of carriers simultaneously².

Among II-VI host semiconductors, ZnO is a versatile and potential candidate³ having a direct wide band gap (3.37 eV), large exciton-binding energy (60 meV), eco-friendly, high transparency, biocompatible and non-toxic. ZnO is promising compound for the gas sensors⁴, light emitting diodes, solar cells, lasers⁵, varistors⁶, photoelectrochemical cells⁷ and cancer therapy⁸.

Improvements in performance of semiconductor materials with better electronic, optical and magnetic properties can be achieved by transition metal dopants, (e.g. Mn^{+2} , Cu^{+2} , Co^{+2} , Fe^{+2} , Ni^{+2})² because of the valency matching of host cations and magnetic ions⁹.

Among all transition metals Mn is more appropriate, since it have maximum magnetic moments. Recently Mn doped II-VI compounds have aroused extraordinary research attempts to open a new door for modern technology and are

highly desired in futuristic spintronics devices¹⁰. In this era, wide band gap DMSs have been broadly studied with the endeavour of making out doped semiconducting materials with ferromagnetic property¹¹.

Compatibility of Mn in ZnO owing its close resemblance of ionic radii with Zn and its thermal solubility is better in ZnO. Mn has electron effective mass ~0.3 m_e (m_e = free electron mass)¹² which results in large injected spins and carriers making Mn:ZnO useful for the spintronics nanodevices^{13,14}. Moreover, Mn doped ZnO is not only applicable for novel magnetic devices but also convalescing the optical properties (absorption and photoluminescence), electrical properties and sensitivity. Mn:ZnO nanostructures are capable to be incorporated in efficient multispectral photodetectors, optical switches and memory devices.

Literature shows that the lattice parameters vary slightly with the Mn content and grain size reduces to nanometers, which is due to the fact that doping stops growth of grains. Bandgap variations are also strongly influenced by the Mn concentration in ZnO¹⁵. The doped ZnO crystals retained its wurtzite structure which is due to Mn ions adjustment at regular Zn sites¹⁶. Doping of Mn in ZnO results in paramagnetic or ferromagnetic behaviour depending on the type and concentration of charge carries⁵.

The properties of the Mn:ZnO thin films are very sensitive to the method adopted and process parameters⁵. DMS thin films can be prepared with various techniques e.g. Pulsed Laser Deposition, RF magnetron sputtering, Spray pyrolysis, Thermal evaporation¹⁷, Molecular beam epitaxy, and Sol gel¹⁸. Sol-gel has selected due to its noticeable advantages e.g. change the material properties by changing the composition of the precursor, ability to control size and shape of the films, low processing temperature, excellent control of microstructures, no need of vacuum, large area can be coated & fabrication is economically best. It is beneficial in permitting Mn doping during growth process of ZnO. Additionally, it is easy to get the materials in volume of gram.

In this paper we have reported that Mn concentration effects on the magnetic and structural properties of ZnO thin films. Addition of dopants change the nanostructure of ZnO thin films at specific concentration as it is also reported by kim et al¹⁹ and Ton-That et al²⁰, they prepared their samples by solid state reaction method and sol-gel respectively. The

present work, thus, shows the use of Mn:ZnO films in magneto-optical and spintronics applications prepared by inexpensive and simple technique.

2. Experimental Details

The sols for ZnO thin films, doped and un-doped, were synthesized by sol-gel method locally by using research grade materials. Zinc acetate $[Zn(CH_3CO_2)_2 \cdot 2H_2O]$ was used as a Zinc source whereas Mn ions were taken from $MnCl_2 \cdot H_2O$. Aqueous medium of triethylamine and isopropylalcohol was used during the synthesis. Un-doped ZnO sol was synthesized by following the procedure mentioned in our previous papers. For doping 0, 5, 15, 20 and 25 mol%. Mn was added in ZnO sol under constant stirring for 30 minutes. Transparent sol was obtained after aging at room temperature for 24 hours.

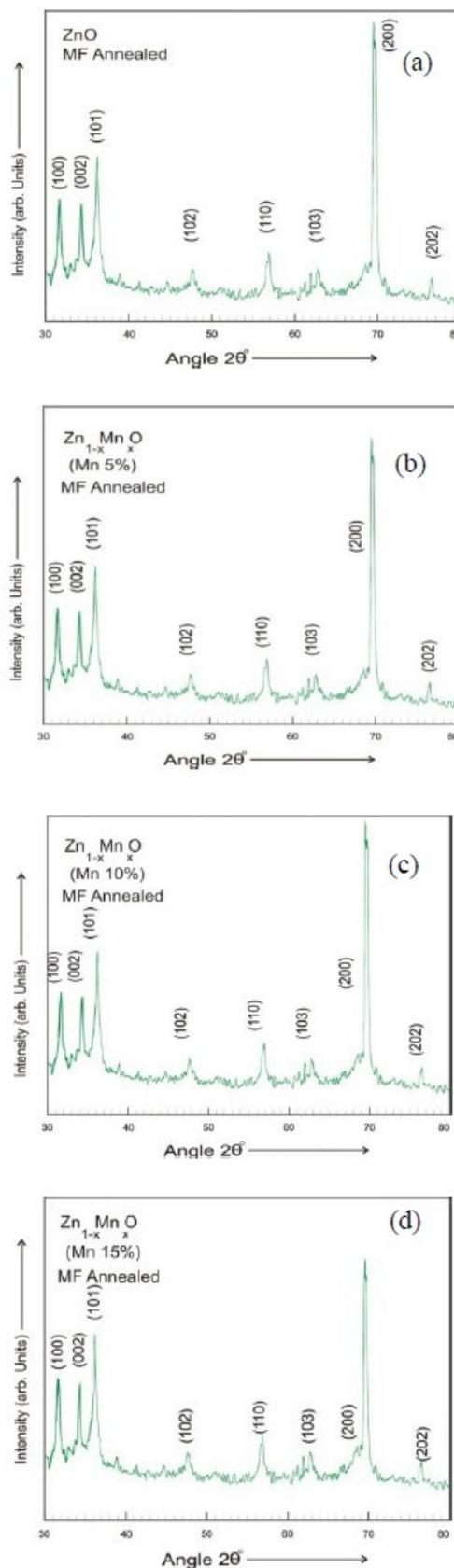
Single crystal Si substrates were used for deposition of un-doped and Mn-doped ZnO thin films. An ultrasonic bath for 30 min with acetone and 20 min with IPA was given to the substrates in order to make them free of any contamination and gas residues on the surface²⁰. The sol was spun onto these substrates at 6,000 rpm for 30 s; thickness of around 150 nm or less was achieved in this way. These samples were dried at room temperature for 20 min and were then subjected to heat treatment at different temperatures for varying times. Un-doped and doped ZnO thin films were characterized structurally with the help of Rigaku D/MAX-IIA X-ray Diffractometer using Ni filtered CuK α ($k = 1.5405 \text{ \AA}$) radiation. The target was operated at 35 kV and 25 mA with a step width of 0.05 on the chart recorder. Lakeshore's 7407 Vibrating Sample Magnetometer (VSM) was used for magnetic characterization of thin films. The data acquisition was performed with a time constant of 0.3 s and for 60 points; this results in around 10 min of data acquisition time under continuous mode.

3. Results and Discussion

Un-doped and doped ZnO thin films were checked for their crystal structure at various stages of polymerization. Figure 1 shows the XRD patterns of MF annealed un-doped and doped thin films. All the films were crystallized at relatively lower temperature of 300°C as compared to the Jiang et al¹⁵.

ZnO formation can be seen in all the samples by the presence of (100), (002) and (101) planes in these XRD patterns [JCPDS card no. 36-1451]. Hexagonal wurtzite structure was observed in the annealed films. Since wurtzite structure is non-centrosymmetric, it is more favorable for inducing and studying magnetism in any material¹⁹. Following Vegard's law the Mn concentration incorporated into ZnO lattice of the 5% sample was estimated to be about 2.6%. Mn has a solid solubility limit of about 13% in ZnO matrix that's why Mn concentration of the 5% (nominal composition) sample is far smaller than the solid solubility limit, suggesting that some Mn ions can be diluted in the ZnO host matrix.

Lattice parameter values of the 0% Mn doped ZnO sample perfectly match with results showed in JCPDS No. 36-1451.



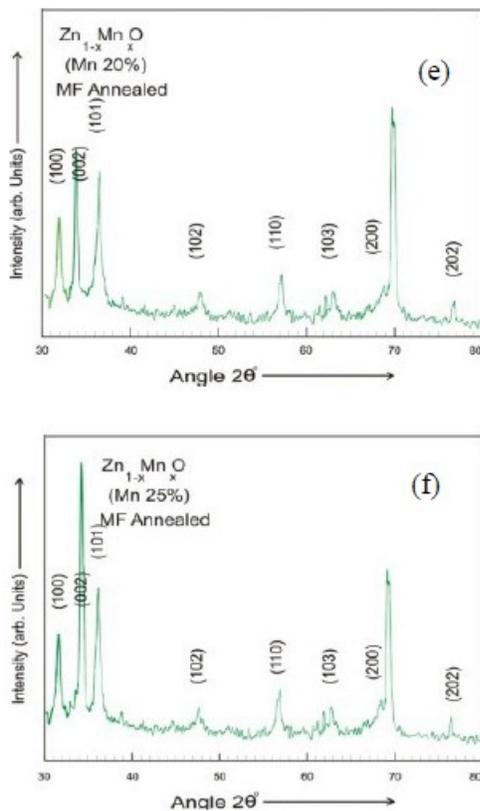


Fig. 1: XRD patterns of MF annealed (a) un-doped and (b-f) Mn-doped ZnO thin films

Upon doping with 5% manganese, the resultant compound maintains a wurtzite structure, but the lattice parameters a and c are both slightly increased in comparison to undoped ZnO. It is consistent with substitution of smaller Zn ions (ionic radius 0.74 \AA^{12}) by larger Mn ions (ionic radius 0.80 \AA^{12}). This effect was also observed in the magnetization plots of un-doped and Mn-doped ZnO thin films. Full Width at Half Maximum was calculated at (002) peaks for all the samples. It was observed that FWHM increased as the Mn concentrations increased.

Figure 2 (a-b) depicts the plots of room temperature magnetization of the as-deposited and annealed (300°C) ZnO thin films respectively.

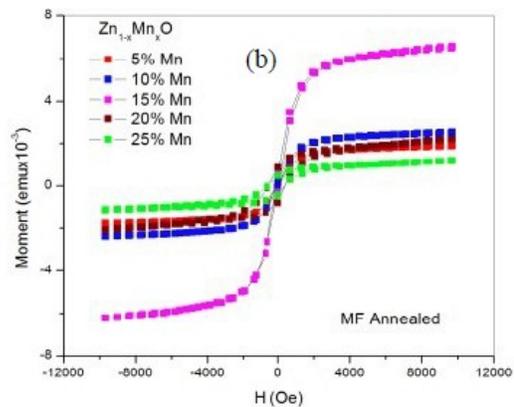
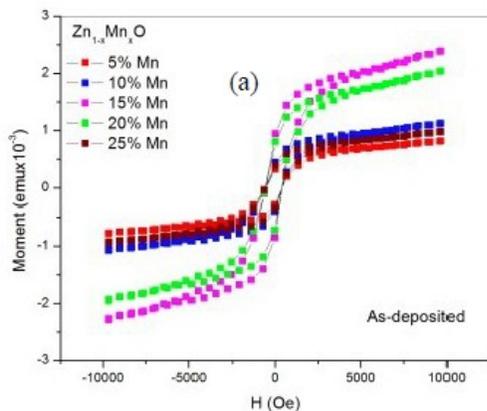
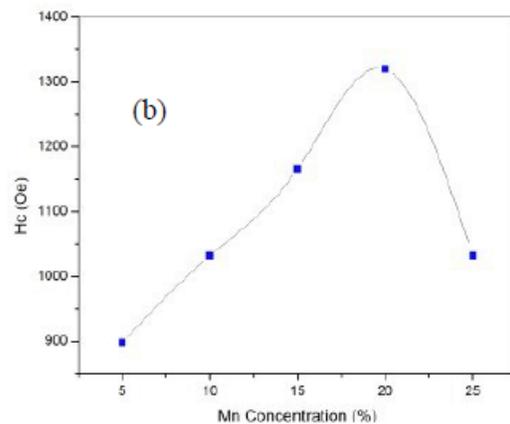
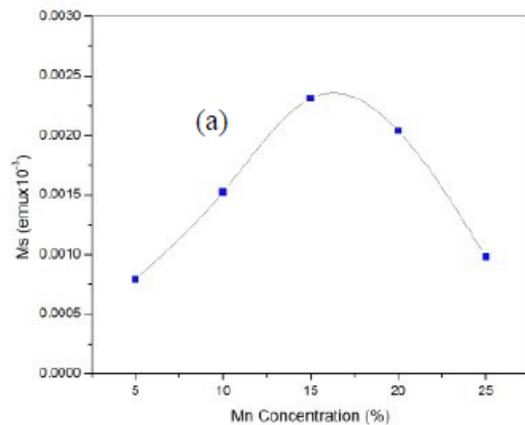


Fig. 2: M-H plots of as-deposited (a) and Mn-doped (b) ZnO thin films

The observed nonlinear magnetization plots show that the films are ferromagnetic even under as-deposited conditions. It can also be seen through these M-H curves that magnetization and squareness increases by increasing the Mn content from 5 – 25%; this is in agreement with the results of Garcia et al.²¹ and Zhou et al.²². It is clear from these plots that all films of Mn-doped ZnO prepared in this work are of ferromagnetic nature.

Figures 3-4 (a-c) showing the variation in coercivity, magnetization and retentivity with Mn concentration before and after MF annealing.



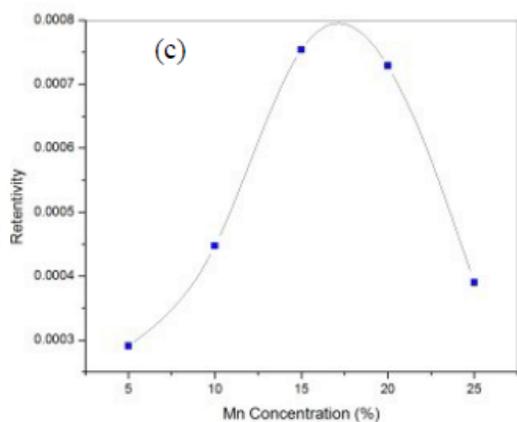


Fig: 3 Variation in (a) Coercivity (b) Saturation Magnetization (c) Retentivity before annealing

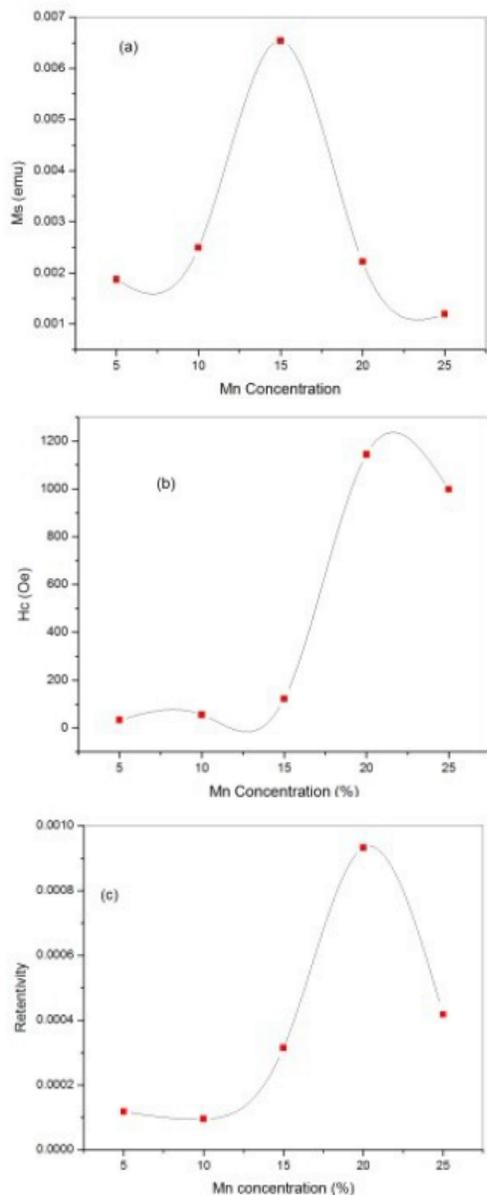


Fig: 4 Variation in (a) Coercivity (b) Saturation Magnetization (c) Retentivity after MF annealing

Coercivity and magnetization increase by increasing Mn concentration 5% to 15%. While decrease in coercivity and magnetization is observed by further increase in Mn concentration. Retentivity of the films is also showing the same behaviour. The decrease in values is due to the fact that at certain percentage of Mn, Zinc oxide nanostructure changes, is also reported kim et al²³.

Figure 4 shows MF annealed samples show an increase in coercivity and retentivity up to 20% Mn concentration while the value of coercivity is less as compared to the as deposited samples. Saturation magnetization have highest value at 15% Mn concentration while decrease for further increase in Mn percentage. The reason is that at higher concentration of Mn, clustering starts.

To check the nano growth, all the samples were characterized through scanning electron microscopy. SEM micrographs (Fig. 5) show the formation of nanorods for the Mn concentration 0 – 20% [Fig. 5a]. Whereas, nanotweezers were observed for 25% Mn concentration as shown in Figure 5(b).

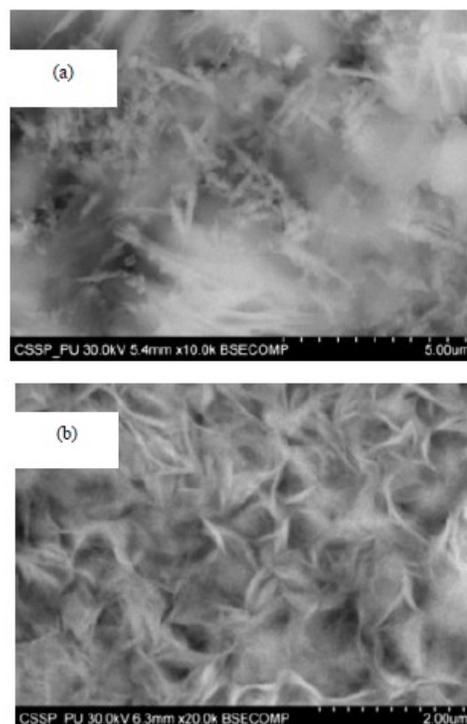


Fig: 5 SEM image of (a) nano rods (0-20% Mn) and (b) nanotweezers (25% Mn)

Variation in structure, as observed by SEM, is given in table-I

Table 3 Variations in central Zn nucleus with Mn concentrations.

SAMPLE	DIMENSIONS	STRUCTURE
ZnO	300nm	Nano-Rods
Zn0.95Mn0.05O0000	200nm	Nano-Rods
Zn0.90Mn0.10O	150nm	Nano-Rods
Zn0.85Mn0.15O	140nm	Nano-Rods
Zn0.80Mn0.20O	100nm	Nano-Rods
Zn0.75Mn0.25O	25nm	Nano-Tweezers

4. Conclusions

Zn_{1-x}Mn_xO thin films have been prepared by Sol gel route. Wurtzite hexagonal structure was observed in un-doped as well as Mn-doped ZnO samples by using XRD. Change in preferred orientation was also noticed by changing the Mn concentration from 20 – 25%. SEM results showed formation of rods for 0-20%. Higher magnetization values and lower shape anisotropy is observed all the samples.

Acknowledgments

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References

- [1] G. R. Li, D. L. Qu, W. X. Zhao and Y. X. Tong, *Electrochem. Commun.* 9, 1661 (2007)
- [2] Q. Liu, R. Deng, X. Ji and D. Pan, *Nanotechnol.* 23, 255706 (2012)
- [3] J. Iqbal, B. Wang, X. F. Liu, D. P. Yu, B. He and R. H. Yu, *New J. Phy.* 11, 063009 (2009)
- [4] R. K. Sharma, S. Patel and K. C. Pargaien, *Nanosci. Nanotechnol.* 3, 035005 (2012)
- [5] S. J. Vethanathan, M. Brightson, S. M. Sundar and S. Perumal, *Mat. Chem. Phy.* 125, 872 (2011)
- [6] S. W. Tan, X. C. Tan, J. Y. Jiang, J. Xu, J. L. Zhang, D. D. Zhao, L. Liu and Z. Y. Huang, *J. Electroanal. Chem.* 668, 113 (2012)
- [7] G. Y. Chai, O. Lupan, E. V. Rusu, G. I. Stratan, V. V. Ursaki, V. Sontea, H. Khallaf and L. Chow, *Sen. Act. A*, 176, 64 (2012)
- [8] C. H. Xu, K. Leung, J. Hu and C. Surya, *Mat. Lett.* 74, 100 (2012)
- [9] W. Wang, Q. Zhao, H. Li, H. Wu, D. Zou and D. Yu, *Adv. Fun. Mat.* 22, 2775 (2012)
- [10] M. M. Baum, S. Polster, M. P. M. Jank and I. Alexeev, *App. Phy. A: Mat. Sci. Proce.* 107, 269 (2012)
- [11] L. Frey and M. S. R. Mehran, *App. Mech. Mat.* 110, 1599 (2012)
- [12] P. F. Tao, J. He, C. J. Liang, J.P. Han, L. Q. Qin and Q. Pang, *Adv. Mat. Res.* 399, 1429 (2012)
- [13] M. J. Akhtar, M. Ahamed, S. Kumar, M. M. Khan, J. Ahmad, and S. A. Alrokayan, *Int. J. Nanomed.* 7, 845 (2012)
- [14] J. Jin, G. S. Chang, Y. X. Zhou, X. Y. Zhang, D. W. Boukhvalov, E. Z. Kurmaev and A. Moewe, *App. Sur. Sci.* 257, 10748 (2011)
- [15] C. S. Chen, T. G. Liu, L. W. Lin, X. L. Xie, Z. W. Ning and X. H. Chen, 189, 643 (2011)
- [16] K. Srinivas, S. M. Rao and P. V. Reddy, *J. Nanopart. Res.* 13, 817 (2011)
- [17] S. Wolf, D. Awschalom, R. Buhrman, J. Daughton, S. Molnar, M. Roukes, A. Chtchelkanova, and D. Treger, *Sci.* 294, 1488 (2011)
- [18] J. Iqbal, X. Liu, A. Majid and R. Yu, *Nov. Mag.* 24, 699 (2011)
- [19] Y. M. Hao, S. Lou, S. M. Zhou, Y. Q. Wang, X. L. Chen, G. Y. Zhu, R. Yuan and N. Li, *J. Nanopart. Res.* 14, 659 (2012)
- [20] B. Pal and P. K. Giri, *J. App. Phy.* 108, 084322 (2010)
- [21] M. A. Garcia, J. M. Merino, E. F. Pinel, A. Quesada, J.D. Venta, M. L. R. Gonzalez, G. R. Castro, P. Crespo, J. Llopis, J. M. Calbet and A. Hernando, *Nano. Lett.* 7, 1489 (2007)
- [22] X. Y. Zhou, S. H. Ge, D. S. Yao, Y. L. Zuo and Y.H.J. Xiao, *J Alloy. Compd.* 463, L9 (2007)
- [23] J. H. Kim, J. B. Lee, H. Kim, W. K. Choo, Y. Ihm and D. Kim, *J. Ferroelec.* 273, 71 (2002)