Research Article

Phase Pure Synthesis and Morphology Dependent Magnetization in Mn Doped ZnO Nanostructures

Murtaza Saleem,¹ Shahid Atiq,² Shahid M. Ramay,³ Asif Mahmood,⁴
Saadat A. Siddiqi,⁵ and Muhammad Ali Shar⁶

¹ School of Science and Engineering (SSE), Lahore University of Management Sciences (LUMS), Opposite Sector U, D.H.A., Lahore Cantt 54792, Pakistan

² Centre of Excellence in Solid State Physics, University of the Punjab, Quaid-e-Azam Campus, Lahore 54590, Pakistan

³ Physics and Astronomy Department, College of Science, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

⁴ Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

⁵ Interdisciplinary Research Centre in Biomedical Materials, COMSATS Institute of Information Technology, Defence Road, Off Raiwind Road, Lahore 54600, Pakistan

⁶ Mechanical Engineering Department, Center of Excellence for Research in Engineering Materials, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

Correspondence should be addressed to Murtaza Saleem; murtaza.saleem@lums.edu.pk

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Zn_{0.95}Mn_{0.05}O nanostructures were synthesized using sol gel derived autocombustion technique. As-burnt samples were thermally annealed at different temperatures (400, 600, and 800°C) for 8 hours to investigate their effect on structural morphology and magnetic behavior. X-ray diffraction and scanning electron microscopic studies demonstrated the improvement in crystallinity of phase pure wurtzite structure of Mn doped ZnO with variation of annealing temperature. Energy dispersive X-ray elemental compositional analysis confirmed the exact nominal compositions of the reactants. Electrical resistivity measurements were performed with variation in temperature, which depicted the semiconducting nature similar to parent ZnO after 5 at% Mn doping. Magnetic measurements by superconducting quantum interference device detected an enhanced trend of ferromagnetic interactions in thermally annealed compositions attributed to the improved structural morphology and crystalline refinement process.

1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted a great deal of interest in recent years due to their applications in modern spintronic devices [1, 2]. One of the major thrusts in ongoing research is the formation of phase pure DMS materials and achievement of ferromagnetism with reasonable magnetization [3, 4]. Theoretical investigations suggest that semiconductors with wide band-gaps are the most potential candidates for this purpose [5, 6]. ZnO has a direct band-gap ($E_g = 3.37$ eV) among semiconductors with hexagonal (wurtzite) crystal structure. Several investigations have been reported by various research groups

to synthesize phase pure transition metals (TMs) doped ZnO DMSs [7–9]. In particular, Mn doped ZnO have been prepared to explore their potential applications in spintronic devices and biomedicine by exploiting their unique magnetic and antibacterial properties [10]. Theoretical prediction for ferromagnetism in Mn doped ZnO has attracted much experimental research interest among these ZnO based DMSs [11]. Many reports exist for achievement of ferromagnetism in these materials [12, 13]. Some exciting results for Mn doped ZnO bulk compositions have been reported. Ferromagnetic phase transition in Zn_{1-x}Mn_xO ($x = 0.05$) sample was observed, which was reported due to the existence of spinel impurity phase like Mn₂O₄ in this system [14]. Li

and coworkers [15] obtained ferromagnetism in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ samples prepared and sintered in nitrogen atmosphere. Room-temperature ferromagnetism was achieved by Sharma et al. [16] in low temperature synthesized thin films and bulk samples of ZnMnO systems. Recently, sintering temperature effect on structural and magnetic properties of Mn doped ZnO bulk system has been studied [17, 18] and ferromagnetic interactions have been detected in a composition sintered up to 700°C . Further, it is also observed that TMs doped ZnO exhibit morphology dependent magnetic behavior, wherein it is recommended that the improved morphology is responsible for enhanced magnetic ordering [19–21]. In addition, emission properties of Mn doped ZnO nanomaterials have also got the attention of scientific community [22]. These studies revealed that preparation technique, thermal annealing, and structural morphology directly influenced the various properties. In addition, the phase pure synthesis of DMS materials with achievement of enhanced magnetization is an essential objective for practical applications in emerging spintronic devices. Hence, this research work is a unique attempt to enhance the magnetic behavior in Mn doped ZnO DMS through improved structural morphology.

The sol gel autocombustion technique offers distinctive synthesis advantages. This ensures the oxide formation and crystallization to create the required and necessary phases of nanostructure materials in a short time [7]. In this work, nanostructures of $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ have been prepared using this technique and afterwards thermally annealed at various temperatures in order to observe their effect on different properties of prepared samples. Thermal annealing significantly affects the structural morphology of material which directly influences the electrical and magnetic properties. Moreover, extensive profound role of impurity phases formed at high-temperature thermal annealing treatment was also observed.

2. Experimental Methods

In order to prepare Mn doped ZnO nanostructures, molar ratios of Zn nitrate $[(\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})]$, Mn nitrate $[(\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})]$, and citric acid $(\text{C}_6\text{H}_8\text{O}_7)$ with 1:1 metal nitrates to citric acid ratio were dissolved in distilled water. All reagents used were of analytical quality. The pH of the solution was maintained at 7 by adding the proper amount of liquid ammonia $[\text{NH}_3]$. The solution was then constantly stirred and dried at 150°C to obtain xerogel. After attaining the xerogel, the temperature was increased to 250°C and the gel was converted into powder by self-combustion. The resulting as-burnt powder was annealed at 400, 600, and 800°C for 8 hours in ordinary environment in a muffle furnace (Ogawa Seiki). As-burnt and thermally annealed samples were characterized by X-ray diffraction (XRD) using a Panalytical X'Pert Pro multipurpose diffractometer (MPD). The X-ray diffractometer was operated at 40 kV and 40 mA with $\text{Cu } K_{\alpha 1}$ radiation ($\lambda = 1.540598 \text{ \AA}$) with step scan size of 0.02. Field emission scanning electron microscopic studies were carried out using S-3700N (Hitachi Japan) equipped

FIGURE 1: XRD spectra of as-burnt and annealed nanostructures of $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$.

with energy dispersive X-ray (EDX) system for morphological and elemental compositional analysis, respectively. Temperature-dependent electrical resistivity was measured using the two-point probe setup. Magnetic properties of samples were obtained from a MPMS XL, Quantum Design, superconducting quantum interference device (SQUID).

3. Results and Discussion

3.1. X-Ray Diffraction (XRD) Studies. Figure 1 shows the XRD patterns of as-burnt and thermally annealed samples at 400, 600, and 800°C for 8 hours in air. The XRD patterns reveal that Mn substitution does not disturb the hexagonal wurtzite type structure and space group of $\text{P6}_3\text{mc}$ of the host ZnO, similar to what has been realized in the previously reported works [18, 23]. The peaks in the diffraction patterns turned out to be more intense and slightly shifted due to thermal annealing. The change in the lattice parameters occurs due to the crystalline refinement process during thermal treatment. However, some additional peak referring to the manganese oxide impurity phase (Mn_3O_4) was detected in the sample annealed at 800°C . No other impurity phase was observed in any other pattern. The calculated values of the lattice parameters a and c were observed to vary between $3.2489\text{--}3.2511 \text{ \AA}$ and $5.2005\text{--}5.2088 \text{ \AA}$, respectively.

Figure 2 demonstrates the variation of lattice parameters with variation of thermal annealing temperature. The average crystallite size was calculated by measuring the full width at half maximum (FWHM) of the most intense diffraction peak (101) in all the patterns using well-known Scherrer formula [7]:

$$D_{h,k,l} = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where “ θ ” is Bragg’s angle, “ λ ” denotes the wavelength ($\lambda = 1.5405 \text{ \AA}$) of $\text{Cu } K_{\alpha}$ radiation, and “ $D_{h,k,l}$ ” depicts the average crystallite diameter and “ β ” the full width at half maximum in

FIGURE 2: Variation in lattice parameters “a” and “c” and crystallite size (inset) with the increase in annealing treatment.

radians. The crystallite size of as-burnt sample was 36.77 nm, which was found to vary as 44.40 nm with the rise in annealing temperature, as illustrated in Figure 2 (inset). The relative decrease in crystallite size at 800°C is attributed to the formation of the manganese oxide impurity phase.

3.2. FESEM and EDX Analysis. Figures 3(a)–3(c) show the FESEM micrograph of as synthesized and annealed samples of Mn doped ZnO nanostructures, respectively. As can be seen in Figure 3(a), the grain size of as synthesized sample is not uniform and turns into agglomerated clusters of highly refined nanometer sized grains when subjected to the thermal annealing treatment. A good proportion of the grains can be seen with small grain size under 100 nm, whereas very large agglomerates having sizes of about 1-2 μm are also present which can be collimated up to 50%. The subsequent thermal annealing on as synthesized powder samples at 400 and 600°C has shown significantly modified morphology. The grains are showing well-defined shapes and edges. It can be inferred that the temperature of thermal treatment significantly affects the crystallinity and uniformity of the structure. The sample annealed at 600°C reveals uniform sized, highly ordered, and phase pure grain structure, which is consistent with the results obtained from XRD analysis. Figure 3(d) shows the EDX pattern revealing the wt% of Zn, Mn, and O elements present in as-burnt $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ sample. The EDX analysis confirms the incorporation of manganese in the ZnO structure and wt% is very nearly equal to the nominal value of Mn in ZnO. EDX quantitative data in Table 1 reveals that the Zn, Mn, and O contents are in quite close agreement with the stoichiometric compositions of the dissolved reactants. Traces of small wt% of C observed in the sample could be originating from the sample stub.

3.3. Electrical Resistivity Analysis. Volume resistance (R_v) as a function of temperature of as-burnt and annealed samples

TABLE 1: EDX quantitative data of as-burnt $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$.

Element	Weight%	Atomic%
C	0.71	2.45
O	22.20	48.29
Mn	4.73	3.56
Zn	72.34	45.70
Total	100.00	100.00

was evaluated and the corresponding DC electrical resistivity values were estimated using the relation $\rho_v = R_v A/L$ [24], where, ρ_v , R_v , A , and L represent the volume resistivity, volume resistance, total area of the sample, and thickness of the pellet, respectively. The values of temperature-dependent DC electrical resistivity measured for all the samples are shown in Figure 4. The overall trend of resistivity decreased with rise of temperature depicting the semiconducting nature of compositions. The lower values of resistivity in annealed samples correspond to the crystalline refinement process associated with the removal of stresses and reduced effect of scattering at crystalline boundaries.

3.4. Magnetic Measurements. Temperature-dependent M/H curves of the samples were obtained in the fixed field range of 10 kOe as shown in Figure 5, indicating clear magnetization in as-burnt and annealed nanostructures. Ferromagnetic interactions in DMS materials can be explained by the RKKY theory [18, 25], according to which the magnetism arises as a result of the exchange interaction between local spin-polarized electrons (such as the electrons of Mn^{2+} ions) and conductive electrons [18, 26]. Figure 5 (inset) shows the inverse susceptibility χ^{-1} plotted as a function of temperature. Extrapolation of the curves towards x-axis specifically at low temperature gives positive values of Weiss temperature revealing the ferromagnetic nature of material. Wang and coworkers [27] have attributed the origin of ferromagnetism in Mn doped ZnO DMS to the existence of secondary phases, like Mn_3O_4 . However, the origin of room-temperature ferromagnetism in ZnMnO DMS is not completely clear yet. Recently, Yang and coworkers [28] confirmed that the origin of room-temperature magnetism could not derive from any impurity or secondary phase. In the meanwhile, decrease in magnetization in sample annealed at 800°C having clusters of impurity phases corroborates the absence of it having any role in the origination of magnetization. It appears that annealing temperature affects the structural arrangement, which in turn results in the improvement of the magnetic properties. The interactions between the Mn^{2+} atoms successfully substituted at the Zn^{2+} sites may contribute to the ferromagnetic behavior of Mn doped ZnO.

It was observed from M/H curves that ferromagnetic interactions appeared at room temperature and showed enhanced values as the temperature was decreased below room temperature. The maximum magnetization was observed at the lowest value of temperature (50 K) which decreased with the rise in temperature. This is in accordance with the Weiss model of ferromagnetism according to which

FIGURE 3: SEM micrographs of (a) as-burnt and annealed samples at (b) 400°C and (c) 600°C (d) EDX pattern of as-burnt $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$.

FIGURE 4: Temperature-dependent resistivity of as-burnt and annealed $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$.

FIGURE 5: Temperature-dependent M/H and (inset) inverse magnetic susceptibility (χ^{-1}) of as-burnt and annealed $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$.

the thermal fluctuations begin to destroy the magnetization. The magnetization values of the samples were observed to increase for the samples annealed up to 600°C . However, this value was decreased in the sample annealed at 800°C . Once again, this is likely due to the presence of paramagnetic or diamagnetic islands of the impurity phases, corroborated by the structural analysis by XRD. Sharma and coworkers [18] reported that the lower values of saturation magnetization might be due to the smaller sizes of crystallites in the samples. As the value of crystallite size increased with the elevated thermal treatment up to 600°C , the corresponding saturation magnetization also increased in concordance with reported results. Crystalline boundaries strongly influence the individual magnetic domain effect and hence are involved in possible interfacial scattering. Strong influence on the magnetization is attributed to low interfacial scattering due to increase in crystallite size with reduced crystalline boundaries.

4. Conclusion

Wurtzite type hexagonal structure was detected by XRD patterns in as-burnt and thermally annealed Mn doped ZnO nanostructures. The values of lattice parameters and crystallite size were changed with varying the annealing temperature due to improvement in morphology and Mn ion substitution at regular sites of Zn. The electrical resistivity measurements confirmed the semiconducting nature of compositions. The magnetic measurements show the ferromagnetic interactions in as-burnt and thermally annealed samples. Thermal annealing affects the structural properties causing changes in saturation magnetization. The sample annealed at 800°C was found to have low magnetization due

to the presence of paramagnetic or diamagnetic effects from manganese oxide impurity phase. Much improved results with respect to saturation magnetization were obtained in more structurally homogeneous composition. It was inferred from these investigations that structural morphology directly influenced the electrical and magnetic properties of DMS materials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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