CHIN. PHYS. LETT. Vol. 29, No. 10 (2012) 106103

Origin of Ferromagnetism in Al and Ni Co-doped ZnO Based DMS Materials *

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(Received 2 July 2012)

$Zn_{0.95}Ni_{0.05}O$ and $Zn_{0.90}Ni_{0.05}Al_{0.05}O$ compositions of nanocrystallites are synthesised using the well recognised auto-combustion technique. The x-ray diffraction patterns demonstrate the phase pure characteristic wurtzite-type crystal structure with space group $P6_3mc$ in both the compositions. The elemental incorporation of Ni and Al contents into the ZnO structure is confirmed by energy dispersive x-ray analysis. The micrographs of scanning electron microscopy show an approximate ordered morphology. The electrical resistivity is observed to decrease with the rising temperature, depicting the characteristic semiconductor behaviour of the samples. The lower values of resistivity and ferromagnetic interactions in the Al-doped sample correspond to an increase of carrier's density. It is observed that the carrier mediated mechanism is mainly responsible for ferromagnetism in ZnO-based diluted magnetic semiconductors.

PACS: 61.46.Hk, 75.50.Pp, 47.70.Pq, 75.75.−c DOI: 10.1088/0256-307X/29/10/106103

Ferromagnetism and its origin in ZnO-based diluted magnetic semiconductor (DMS) materials are topics of great interest due to controversy among the research community.[1−4] It was found that ferromagnetic behaviour is strongly dependent upon the method of preparation, experimental conditions and the structural homogeneity.[5−7] According to recent controversial reports, ferromagnetism might be associated with direct exchange interactions among magnetic atoms in structure or the secondary phases of magnetic species such as NiO_2 and Ni_2O_3, etc.,[1] vacancy induced mechanism,[2] the Zener field model,[8] and Rudermann Kittel Kasuaya Yoshida (RKKY) interactions.[9,10] Some of the controversial aspects like ferromagnetism due to secondary phases and transition metal clustering can be eliminated with the formation of a phase pure material. In the case of dilute doping of magnetic elements, it seems very difficult that magnetic atoms lie very close to each other in structure. In this way, short ranged direct exchange magnetic interactions among Ni-Ni atoms can also be ignored. ZnO has a natural n-type conductivity and is very hard to produce in p-type form.[11] The possibility of the Zener field model associated with the hole-mediated mechanism is surely not responsible for ferromagnetism in these materials. The most prominent mechanism is RKKY that corroborates with the carriers (electrons) mediated interactions and can be studied by varying the concentration of carriers in the structure. The partial substitution of Al^{3+} atoms at Zn^{2+} sites would significantly enhance the concentration of carriers[12] and the carrier-mediated mechanism can be verified in this way. In this work, an attempt has been made to synthesise the phase pure compositions of DMS materials. The origin of ferromagnetism has been studied by varying the concentration of carriers with Al^{3+} substitution at Zn^{2+} sites in the ZnNiO system. It is suggested that this work is a fair contribution towards resolving the recent ongoing controversy about the origin of ferromagnetism in ZnO-based DMS materials.

Nano-crystalline $Zn_{0.95}Ni_{0.05}O$ and $Zn_{0.90}Ni_{0.05}Al_{0.05}O$ samples were synthesised using the auto-combustive sol-gel technique. All starting chemicals including zinc nitrate $[Zn(NO_3)_2{\cdot}6H_2O]$, nickel nitrate $[Ni(NO_3)_2.6H_2O]$, aluminum nitrate $[Al(NO_3)_3{\cdot}6H_2O)]$ and glycine used, were of analytical research grade purity. The glycine was used here as a fuel agent. The metal nitrate (MN) to glycine ratio was taken as 1:2. The calculated molar quantities of the starting chemicals were dissolved in 150 ml deionised water. This aqueous solution was mixed under continuous stirring for about one hour. The approximate pH value of the net solution was observed to be 3.5. The brownish colour of the xerogel chemical solution was obtained through vigorous stirring and heating at 200℃ on a very sensitive hot plate. As soon as the xerogel was attained, the temperature was raised to 300℃. The gel was then converted into a fine powder after an intense explosive exothermic reaction. X-ray diffraction (XRD) patterns were obtained using a Panalytical X'Pert Pro multipurpose diffractometer (MPD) for structural analysis. The diffractometer was operated at 40 kV and 40 mA using Cu $K_{\alpha 1}$ radiation having $\lambda = 1.540598$ Å with a step scan size of 0.02. The morphological and compositional analysis was carried out using an S-3700 N (Hitachi Japan) scanning electron microscope (SEM) equipped with

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an energy dispersive x-ray (EDX) system. Magnetic measurements were performed using the Lakeshore-7404 vibrating sample magnetometer (VSM) in an in-plane applied magnetic field of ±10 kOe. A two-point probe setup was used to measure the electrical properties of the pelletised samples sintered at 300℃ for three hours.

ZnO is a quite moderate material as it retains its wurtzite hexagonal crystal structure when doped with dilute amount of magnetic elements.[13] The same fact has been confirmed in the XRD patterns as shown in Fig. 1. The Ni or (Ni+Al) substitution does not disturb the space group $P6_3mc$ and crystal structure of the host ZnO, as no impurity peak or other phase was detected. The peaks were broadened and less intense in Al-doped composition, which might be due to the difference in ionic radii of the dopants. In addition, the doping of Al affected the values of the lattice constants a and c, which were found to vary from 3.2886 to 3.2419 Å and from 5.3911 to 5.2304 Å, respectively, as shown in Table 1. The breadth of the characteristic diffraction peaks is an indication of the lower size of crystallites. The crystallite size has been estimated from the x-ray peak broadening, considering the most intense diffraction peak (101) for all the samples, using the Scherrer formula.[14] The evaluated crystallite size of $Zn_{0.95}Ni_{0.05}O$ composition was 53.33 nm, which was decreased to 42.97 nm with additional doping of Al as obvious in Table 1, which was again an evidence of the substitution of Al^{3+} at the Zn^{2+} sites in the ZnO matrix.

Table 1. Calculated values of lattice parameters and crystallite sizes.

Sample	Lattice constants (Å)	Crystallite size (nm)
$Zn_{0.95}Ni_{0.05}O$	a=3.2886 c=5.3911	53.33
$Zn_{0.90}Ni_{0.05}Al_{0.05}O$	a=3.2419 c=5.2304	42.97

Table 2. EDX quantitative measurements of $Zn_{0.95}Ni_{0.05}O$ and $Zn_{0.90}Ni_{0.05}Al_{0.05}O$.

$Zn_{0.95}Ni_{0.05}O$			$Zn_{0.90}Ni_{0.05}Al_{0.05}O$		
Element	wt%	at.%	Element	wt%	at.%
C	0.81	2.65	C	0.95	2.77
O	19.93	49.08	O	22.47	48.91
Ni	5.10	3.57	Ni	6.73	3.98
Zn	74.16	44.70	Zn	65.73	39.01
			Al	4.12	5.33
Total	100.00	100.00	Total	100.00	100.00

SEM micrographs of $Zn_{0.95-x}Ni_{0.05}Al_xO$ (x = 0, 0.05) show an approximate ordered morphology, as shown in Figs. 2(a) and 2(b). The morphology of the Al-doped sample detected small sizes of the grains than in the other compositions, which could be correlated with the smaller sizes of the crystallites in this composition by XRD analysis. XRD patterns cannot indicate the existence of Ni and Al contents in the synthesised compositions in the case of an exact substitution of these elements at the Zn sites. EDX spectra for $Zn_{0.95-x}Ni_{0.05}Al_xO$ (x = 0, 0.05) samples for qualitative and qualitative elemental compositional measurements are shown in insets in Figs. 2(a) and 2(b). The characteristic peaks recorded in the inline mode of the EDX spectra clearly detected the presence of Zn, Ni, Al and O contents in quite close agreement to the dissolved reactants, which confirmed the incorporation of Ni and (Ni+Al) into the ZnO matrix. The nominal percentage values of various contents for both compositions are mentioned in Table 2.

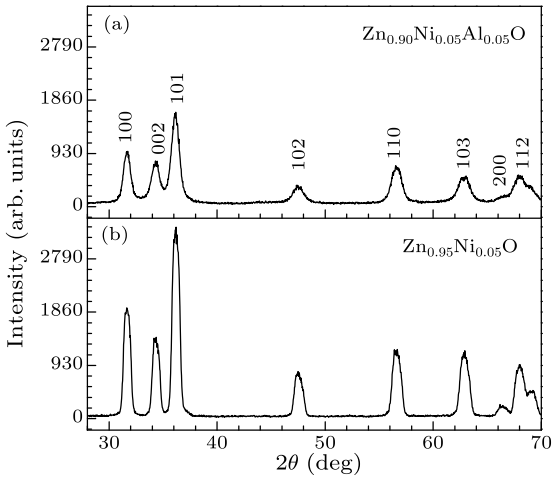


Fig. 1. XRD patterns of $Zn_{0.95}Ni_{0.05}O$ and $Zn_{0.90}Ni_{0.05}Al_{0.05}O$.

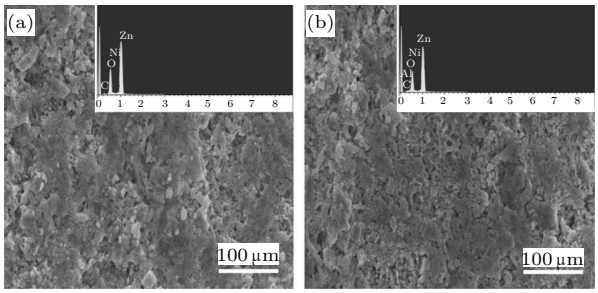


Fig. 2. SEM micrographs and EDX spectra of (a) $Zn_{0.95}Ni_{0.05}O$ and (b) $Zn_{0.90}Ni_{0.05}Al_{0.05}O$.

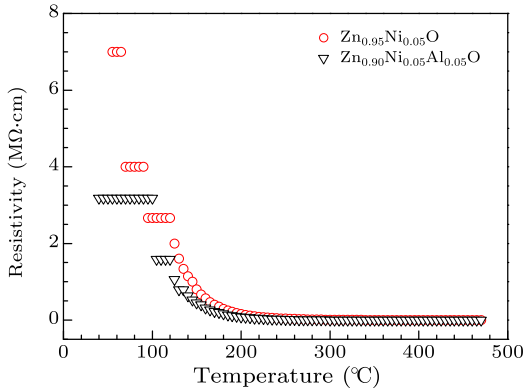


Fig. 3. Temperature-dependent resistivity of $Zn_{0.95}Ni_{0.05}O$ and $Zn_{0.90}Ni_{0.05}Al_{0.05}O$.

The temperature-dependent volume resistance R_v of all the samples was measured and the corresponding values of resistivity were calculated using the relation

$\rho_v = R_v A/L$,[15,16] where ρ_v is the volume resistivity, R_v the measured volume resistance, A the cross-sectional area of the samples (in pellet form) and L is the thickness of the pellet across which the volume resistance has been measured. Figure 3 shows the values of temperature-dependent dc electrical resistivity evaluated for both the samples. It can be observed that the values of resistivity decrease with the rising temperature. However, lower values of resistivity in the Al-doped ZnNiO sample refer to the increase of free carriers due to the substitution of Al^{3+} at the Zn^{2+} sites in the matrix. The overall trend observed in both samples is that the values of dc electrical resistivity decrease with the rising temperature, confirming the semiconductor behaviour.

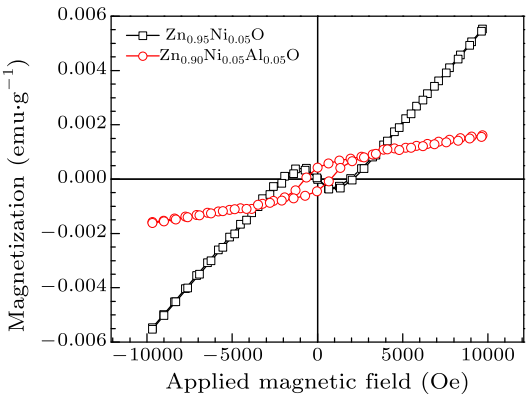


Fig. 4. Field-dependent M–H loops of $Zn_{0.95}Ni_{0.05}O$ and $Zn_{0.90}Ni_{0.05}Al_{0.05}O$.

The magnetic properties of $Zn_{0.95-x}Ni_{0.05}Al_xO$ ($x = 0$, 0.05) samples were investigated using a VSM. Figure 4 shows the room-temperature (RT) field-dependent magnetic hysteresis (M–H) loops, which clearly indicate the presence of ferromagnetism in the Al-doped composition. However, no ferromagnetic interactions can be observed in the $Zn_{0.95-x}Ni_{0.05}O$ composition. The simple substitution of Ni^{2+} at regular sites of Zn^{2+} could not contribute any role in the variation of free carriers in the structure. In addition, it appeared that both compositions have no secondary or impurity phase, which might be useful to subtract any dominant role of these phases in existence of ferromagnetic interactions. Further, the direct interactions among Ni-Ni atoms in the structure are very short ranged. It is not feasible that Ni atoms occupy the significant adjacent sites in the case of its dilute doping in the ZnO matrix and hence to produce the ferromagnetic behaviour due to these interactions. According to the RKKY theory,[17–19] the ferromagnetic interactions in DMS materials are usually produced due to the exchange interaction between local spin-polarised electrons (such as the electrons of Ni^{2+} ions) and conductive electrons or free carriers. It is revealed that the presence of free carriers in the matrix has a substantial impact for the introduction of ferromagnetic behaviour in Ni-doped ZnO materials. The co-doping of Al^{3+} enhances the free carriers up to a considerable extent, as confirmed by the reduced values of resistivity in the $Zn_{0.90}Ni_{0.05}Al_{x0.05}O$ composition. Therefore, it can be concluded from these investigations that a carrier's mediated RKKY-type interactions are mainly responsible for ferromagnetism in magnetic-element-doped ZnO-based DMS materials.

In summary, $Zn_{0.95}Ni_{0.05}O$ and $Zn_{0.90}Ni_{0.05}Al_{0.05}O$ nanocrystallites have been successfully synthesised in phase pure form using the auto-combustive sol gel technique. As revealed by XRD analysis, both the compositions have phase pure wurtzite-type crystal structure. SEM micrographs show approximate-order morphology of the samples. The incorporation of Ni and Al contents in a ZnO matrix with nearly equal percentage values of dissolved reactants is confirmed by EDX analysis. Temperature-dependent resistivity is observed to decrease with the increasing temperature, depicting the semiconducting nature of both the compositions. The lower values of resistivity in the Al-doped composition demonstrate an enhancement of free carriers. The magnetic measurements indicate the ferromagnetic interactions in the Al-doped composition attributable to the existence of carrier-mediated RKKY mechanism.

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