

Structure, Optical, and Room-Temperature Ferromagnetic Properties of Pure and Transition-Metal-(Cr, Mn, and Ni)-Doped ZnO Nanocrystalline Films Grown by the Sol–Gel Method

W. W. Li,[†] W. L. Yu,[†] Y. J. Jiang,[‡] C. B. Jing,[‡] J. Y. Zhu,[†] M. Zhu,[§] Z. G. Hu,^{*,†} X. D. Tang,[†] and J. H. Chu[†]

Key Laboratory of Polar Materials and Devices, Ministry of Education, Department of Electronic Engineering, East China Normal University, Shanghai 200241, People's Republic of China, College of Materials and Engineering, Qingdao University of Science and Technology, Qingdao 266042, People's Republic of China, and Department of Physics, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received: April 8, 2010; Revised Manuscript Received: June 4, 2010

Transition-metal-(Cr, Mn, and Ni)-doped zinc oxide (ZnO) with the concentration of 2.5% and pure ZnO nanocrystalline (nc) films have been fabricated on quartz substrates by the sol–gel method. The X-ray diffraction analysis shows that the films are polycrystalline with the wurtzite phase. The E_{2}^{high} phonon mode shifts about 7 cm^{-1} with different transition metals, and the $A_1(\text{LO})$ phonon mode redshifts 4 cm^{-1} with the ionic radius of doping elements. From the transmittance spectra, all films are highly transparent in the visible region and exhibit Urbach tail states in the ultraviolet range because of the crystalline defects and grain boundaries. The optical band gap of the films decreases with increasing the orbital occupation numbers of 3d electrons due to the orbital splitting of magnetic ions. It was found that a distinct and strong excitonic transition appears beyond the fundamental absorption region at room temperature. Ultraviolet and near-infrared electronic transitions can be observed and show the strong relationship with the transition metal doping. Moreover, orange, yellow and red luminescences strongly depend on the doping elements owing to different oxygen vacancy, oxygen interstitial, and surface morphology. Magnetic measurement results reveal that all the transition-metal-doped nc-ZnO films show the well-defined ferromagnetic features at room temperature. In particular, the nc-ZnO film doped with Mn shows the largest saturation magnetic moment, which agrees well with the theoretical predication. The ferromagnetic properties could be derived from the doping of magnetic ions, intrinsic defects, interfaces, and grain boundaries in the transition-metal-doped nc-ZnO materials.

I. Introduction

The idea of utilizing the spin of carriers in novel spintronic devices has led to efforts in fabricating and investigating appropriate new materials during the past years. It is essential to develop semiconductors with ferromagnetically polarized carriers at room temperature (RT) so that the spin as well as charge of the carriers can be coupled with an external magnetic field.¹ For this reason, diluted magnetic semiconductors (DMS) have attracted considerable interest because of their potential applications in spintronic, optoelectronic, and magnetoelectronic devices.^{2–5} In particular, many investigations have been focused on 3d isovalent transition-metal-doped zinc oxide (ZnO:TM), which was amplified by theoretical predictions and experiments suggesting that ferromagnetism (FM) with Curie temperatures above RT could be obtained.^{2,3} ZnO has wide optical band gap (OBG) of about 3.37 eV, high optical transparency, good electrical conductivity, and large exciton binding energy of 60 meV at RT, which make it promising as an alternative host semiconductor.^{6,7} Furthermore, the Zn atoms are tetrahedrally coordinated to four oxygen atoms, where Zn 3d electrons hybridize with the oxygen 3p electrons. Magnetic TM ions (Cr, Mn, Fe, Co, Ni, etc.) substituting the Zn cation sites could

incorporate FM in ZnO. The coupling of localized TM d electrons with the ZnO band gap leads to a number of exciting properties such as magnetoelectronic, optoelectronic, and magneto-optical effects.⁴ On the other hand, it is well-known that films, which can be deposited directly on diversified substrates, are expected to yield better sensitivity and faster response than the equivalent bulk single crystal. It suggests that some further investigations on ZnO:TM films are necessary to clarify the physical properties, which can provide the theoretical and experimental supports for ZnO-based DMS device applications.

Optical, electrical, and magnetic properties of ZnO:TM materials, which could be directly correlated with the electronic band structure due to the density-of-states (DOS), play an important role in the design, optimization, and evaluation of ZnO-based DMS optoelectronic devices. Up to date, these properties have been extensively studied by many groups for several years. Kim et al. reported that the OBG of Co-doped ZnO films increases with Co concentration.⁴ Singh et al. suggested that the electrical resistivity of Ti-, V-, Fe-, and Ni-doped ZnO bulk sample decreases as compared to undoped ZnO.⁸ Yu et al. found that the FM behavior of Ni doped ZnO (ZnO:Ni) films only occurs when Ni content is low at RT.⁹ The doping of TM can induce more mismatches and defects in the lattice structure and further affect its optoelectronic properties. However, there are few systematical reports concerning the relationship among different TM dopants, lattice vibrations, and electronic transitions properties for ZnO:TM nanocrystalline (nc)

* To whom correspondence should be addressed. E-mail: zghu@ee.ecnu.edu.cn.

[†] East China Normal University.

[‡] Qingdao University of Science and Technology.

[§] Shanghai Jiao Tong University.

films. Among many fabrication techniques, the sol–gel technique has been extensively used in film deposition. It is efficient in producing thin, uniform, transparent, and multicomponent oxide layers with many structures on various substrates.¹⁰ In addition, it was reported that the sol–gel technique can be applied to grow ZnO with the well-defined DMS behavior. The large coercivity (600 Oe) and saturation magnetization (1.2 emu/g) have been observed from 5% Co doped ZnO bulk sample prepared by sol–gel method.¹¹ There are some spectral techniques to determine optical properties of semiconductor film materials. Photoluminescence (PL) spectra are very sensitive to the crystalline quality, energy level of the impurities, and the presence of defects.¹² Transmittance spectra can directly provide absorption characteristics and band tail state behavior. On the other hand, many experimental and theoretical works have focused on the relationship among defects, PL, and magnetic properties. One proposed that the intrinsic defects are responsible for the visible luminescence bands.¹³ The interaction among the defects, 3d ions, grain boundaries, Zn interstitials (Zn_i), and/or exchange interactions between unpaired electron spins arising from the oxygen vacancies (V_o) at the surfaces of nanoparticles could contribute to the FM properties.^{13,14} However, the mechanisms of visible luminescence band and the origin of FM for nc-ZnO:TM films still remain a controversial topic. Therefore, it is desirable to carry out a delicate study regarding the essential properties and their relation of high quality ZnO:TM films using above spectral techniques.

In this paper, the fabrication, structure, and lattice vibrations of nc-ZnO:TM with TM concentration (C_{TM}) of 2.5% and pure nc-ZnO films on quartz substrates have been studied. The luminescence properties, variation trend of OBG, and excitonic transitions have been investigated by PL and transmittance spectra. Especially, the effects from different TM dopants on the optical and magnetic properties have been discussed in detail.

II. Experimental Details

Film Growths. The nc-ZnO:TM films on quartz substrates were prepared by the sol–gel technique. Double-side polished quartz wafers, which were selected for the ultraviolet (UV) transmittance measurements, were used as the substrates. It should be emphasized that all chemical materials and organic reagents used in the experiments are analytical pure and are utilized without further purification. Therefore, the effects from impurities in the solution could be neglected, as compared with the TM doping concentration. Initially, 30 mL of deionized water was mixed with 40 mL of ethanol in a glass beaker. Then 0.03 mol zinc acetate, 0.05 mol urea, 0.05 mol acetylacetone, and corresponding quantity $TM(Ac)_2$ ($TM = Cr, Mn, \text{ or } Ni$) were added into the solutions. After constant stirring at 50 °C for 25 min, the solution was ripened at 85 °C for 10 h to obtain sol. The as-synthesized sol was deposited by spin-coating method at the speed of 3000 rpm for 40 s. Each layer was dried at 100 °C for 5 min and then annealed at 700 °C for 10 min in an ambient atmosphere by a rapid thermal annealing procedure. The aforementioned spin-coating, drying, and annealing were repeated ten times in order to obtain the films with the desired thickness.

XRD, AFM, Spectral, and Magnetism Measurements. The crystalline structure of the pure and nc-ZnO:TM ($C_{TM} = 2.5\%$) films was analyzed by X-ray diffraction (XRD) using Cu $K\alpha$ radiation (D/MAX-2550 V, Rigaku Co.). In the XRD experiments, a vertical goniometer (model RINT2000) was used, and continuous scanning mode ($2\theta/\theta$) was selected with an interval of 0.02° and scanning rate of $10^\circ/\text{min}$. The surface morphology

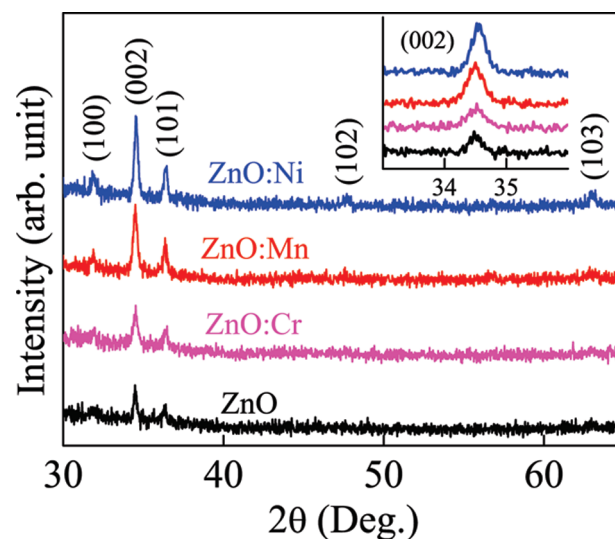


Figure 1. XRD patterns of the undoped and ZnO:TM ($C_{TM} = 2.5\%$) nanocrystalline films. Note that the intensities of all peaks increase with the ionic radius of dopants. The inset shows the enlarged region of the (002) diffraction peak.

was investigated with the contacting mode by atomic force microscopy (AFM) (Dimension 3100, Veeco). Raman scattering experiments were carried out by a micro-Raman spectrometer (Jobin-Yvon LabRAM HR 800 UV) using resonant Raman spectral method with a 325 nm He–Cd laser as the excited light.

PL spectra were recorded with the same spectrometer and laser source with the excitation power of 30 mW. Near-normal far-infrared (FIR) reflectance spectra ($\sim 10^\circ$) were measured over the frequency range of $300\text{--}600\text{ cm}^{-1}$ using Fourier transform infrared (FTIR) spectrometer (Bruker VERTEX 80v). A DTGS detector and $6\text{-}\mu\text{m}$ -thick Mylar beam splitter were employed for the measurement with a spectral resolution of 2 cm^{-1} . Aluminum (Al) mirror, whose absolute reflectance was directly measured, was used as reference for the reflectance spectra. The optical transmittance were recorded with a double-beam UV-IR spectrophotometer (PerkinElmer Lambda 950) at the photon energy range from 1.5 to 6.5 eV (190–820 nm) with a spectral resolution of 2 nm. The magnetic properties of the films were obtained by a physical property measurement system (Quantum Design PPMS-9). Note that the samples were at RT for all measurements and no mathematical smoothing has been performed on the experimental data.

III. Results and Discussion

Structural Analysis. The XRD patterns of the pure and nc-ZnO:TM ($C_{TM} = 2.5\%$) films prepared on quartz wafers are shown in Figure 1. As can be seen, all samples exhibit a single phase with the hexagonal wurtzite structure. Besides the strongest (002) diffraction peak (about 34°), some other weaker peaks (100) and (101) can be found, which illustrates that the films are polycrystalline with different orientations. The full width at half-maximum (fwhm) and peak positions of the (002) diffraction peak, which were obtained by the Gaussian curve fitting, are listed in Table 1. It can be found that the fwhm of the (002) peak is different with the nanocrystalline films. There is no evident shift in the peak positions while the diffraction peaks become more strong and sharp with the ionic radius of doping elements due to the better crystallization. Generally, the XRD technique is frequently applied to estimate the grain sizes and lattice parameters of film materials.^{15–17} The calculated c -axis lattice constant from the (002) plane for all samples is

TABLE 1: Calculated fwhm, Peak Positions, *c*-Axis Lattice Constants, and Grain Sizes from the (002) Diffraction Peak^{a,b}

samples	fwhm (deg)	peak position (2θ , deg)	lattice constant (\AA)	grain size (nm)	E_2^{high} (cm^{-1})	A_1 (LO, cm^{-1})	E_1 (TO, cm^{-1})
ZnO	0.263	34.499	5.195 ± 0.002	35 ± 1	438	569	414
ZnO:Cr	0.368	34.509	5.194 ± 0.002	25 ± 1	439	569	415
ZnO:Mn	0.303	34.497	5.196 ± 0.002	31 ± 1	432	566	413
ZnO:Ni	0.268	34.553	5.187 ± 0.002	35 ± 1	432	565	413

^a The photon mode frequencies obtained from Raman scattering and far-infrared reflectance measurements of the undoped and nc-ZnO:TM ($C_{\text{TM}} = 2.5\%$) phonon films. ^b The uncertainty errors of the lattice constant and grain size are given with (\pm).

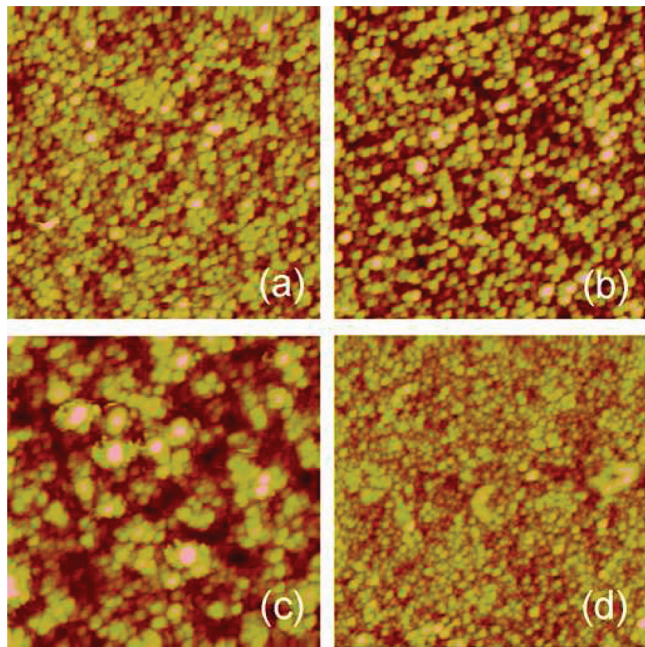


Figure 2. AFM two-dimensional images of (a) ZnO:Ni, (b) ZnO:Mn, (c) ZnO:Cr, and (d) pure ZnO films, respectively. Note that the scale height is 100 nm and the measured area is $5 \times 5 \mu\text{m}^2$.

about 5.19 \AA . The result is in good agreement with the previous reports on ZnO:Ni film.⁹ The grain size r can be calculated from the (002) peak according to the well-known Scherrer equation: $r = K\lambda/\beta \cos \theta$, where $K \approx 1$ is the shape factor, $\lambda = 1.540 \text{ \AA}$ is the average wavelength of Cu K α radiation, $\beta^2 = (\text{fwhm})^2 - b^2$, b is a factor to compensate for the line broadening effect, and θ is the diffraction angle.¹⁷ According to the equation, the uncertainty error in the calculation may come from the estimation of β and peak position θ . Note that the crystal strain, which can slightly broaden the XRD peaks, has been considered in the estimation of the fwhm. Also the evaluation of β , which is generally a result of the combined effects from the crystallite size and instrumental broadening, has been taken into account the line broadening in the XRD measurements. For comparison, the *c*-axis lattice constants, grain sizes, and their uncertainty errors are also listed in Table 1. The calculated grain sizes change with different dopants and the ZnO:Cr film has a minimum grain size (25 nm). The smaller grain size indicates that there are more number of grain boundaries and the total amount of nonrecombination centers inside films.¹⁸ Therefore, it can be concluded that the different TM dopants can result in the variations of film crystallization.

Surface Morphology. Figure 2 shows the surface morphology of pure and nc-ZnO:TM films for different dopants. Obviously, the substrates are covered with nanoparticles of different sizes and the surface morphology of the films is significantly affected by the doping elements. It can be concluded that the films have the nanocrystalline growth pattern. Furthermore, the surfaces of all films are compact except for

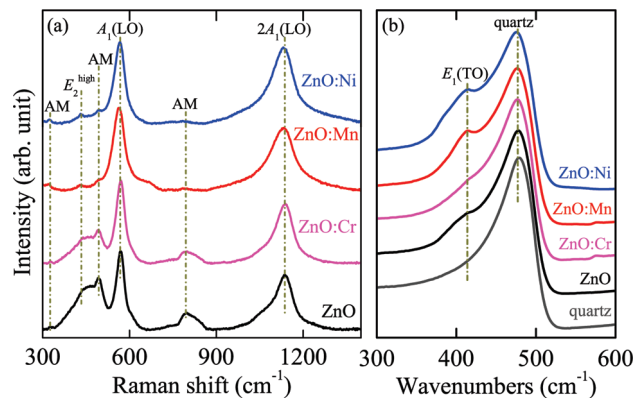


Figure 3. Raman scattering (a) and far-infrared reflectance (b) spectra of the undoped and ZnO:TM films. Note that the dotted lines indicate the lattice vibration modes and the abbreviation “AM” denotes additional mode.

the Cr-doped ZnO (ZnO:Cr) film, which shows a porous surface and some voids appear on the surface. Some large islands, which are found from the undoped ZnO film, could be ascribed to the agglomerations of smaller grains. Nevertheless, there is no evident island for the ZnO:TM films, which indicates that the TM doping might help for nanocrystalline films growth. The remarkable discrepancy of the surface morphology can result in the different optical and electrical properties of the nc films.

Lattice Vibrations. A precise knowledge of the vibration modes may help to understand the thermal as well as electrical properties in terms of low- and high-field carrier transports.² The Raman spectra of the films are presented in Figure 3a. As an example, two typical phonon mode frequencies, and their assignments are also listed in Table 1. The first sharp peak can be assigned to the A_1 longitudinal optical (LO) phonon mode. The peak frequency is lower than that reported by Du et al. (574 cm^{-1}) due to different crystallinity.⁵ As can be seen from Table 1, the A_1 (LO) phonon mode redshifts about 4 cm^{-1} toward the lower energy side with the ionic radius of doping elements. This is because the free carrier concentration changes with the ionic radius of doping elements and further results in the varied frequencies of LO-plasmon coupling modes.¹⁹ Note that the $2A_1$ (LO) phonon mode can be observed in the Raman spectra as well. It is associated with the second-order response of the A_1 (LO) mode. It should be emphasized that the relatively integrated intensity ($I_{A_1(\text{LO})}/I_{2A_1(\text{LO})}$), which reflects the coupling strength between the electron and LO phonon, decreases with the ionic radius of doping elements. The scattering intensity in resonant Raman spectra correlates closely with laser lines, grain size, and band gaps of films,⁵ which is consistent with the AFM results.

Besides the normal vibration modes, three additional modes (AM) can be observed at about 326 , 491 , and 792 cm^{-1} , which could be attributed to the multiple-phonon scattering process in the disorder lattice.²⁰ Interestingly, the intensities of the two AMs located at about 491 and 792 cm^{-1} decrease with the ionic radius of doping elements. This is because the better crystal-

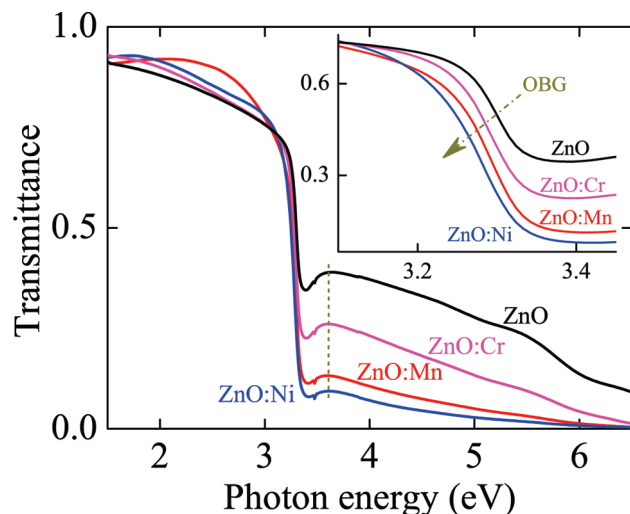


Figure 4. Transmittance spectra of the undoped and ZnO:TM films grown on quartz substrates in the photon region of 1.5 to 6.5 eV. The dashed line indicates the strong excitonic transition. The enlarged fundamental band gap region of 3.1–3.45 eV is plotted in the inset. Note that the arrow shows the OBG variation trend.

lization of the film could decrease the multiple-phonon scattering process in the disorder lattice. Hence, the intensity of the (002) diffraction peak from the XRD measurement and two AMs from Raman experiment show a different variation trend. Nevertheless, the separate variations are strongly related to the TM doping and agree well with the doping effect, which reflects the crystalline quality of the nc-ZnO:TM films. The nonpolar E_2^{high} phonon mode can be detected at about 435 cm^{-1} . It is related to the band characteristic of the wurtzite phase. Note that the values of the Mn doped ZnO (ZnO:Mn) and ZnO:Ni films are slightly less than the previous reports (438.5 and 437 cm^{-1}).^{20,21} This discrepancy can be ascribed to different doping method and crystalline orientation. It was reported that the E_2^{high} phonon mode is also related to the level of V_o in the lattice.²² Therefore, the fact that the E_2^{high} phonon mode shifts about 7 cm^{-1} with different films reveals that the doping of TM can change the V_o level. The phonon mode emerging at about 326 cm^{-1} is identified as $(E_2^{\text{high}} - E_2^{\text{low}})$.²⁰ Unfortunately, the E_2^{low} mode can not be detected in the present work owing to the limit of experimental spectral region. However, the average vibration frequency of E_2^{low} is evaluated to about 109 cm^{-1} , which can be obtained from the values of $(E_2^{\text{high}} - E_2^{\text{low}})$ and E_2^{high} . This value is slightly larger than that reported for nc-ZnO films (102 cm^{-1}).²³

IR reflectance spectroscopy can be used to estimate the phonon frequency and carrier mobility of semiconductor materials. As compared with the Raman technique, IR reflectance method is based on the potentially different selection rule and the penetration of the exciting radiation.²⁴ Figure 3b depicts the FIR reflectance spectra of the films. The vibration mode at about 477 cm^{-1} originates from the quartz substrate. In particular, a shoulder peak appearing at about 414 cm^{-1} for all films could be assigned to the E_1 transverse optical (TO) phonon mode, which can reflect the strength of the polar lattice bonds.²⁵ Note that the value is slightly higher than that from previous investigations (409 cm^{-1}).²⁵ The weaker intensity of E_1 (TO) phonon mode for the ZnO:Cr film might be ascribed to the porosity of the film. This is because the increasing of porosity may induce more scattering processes and less IR reflectivity.

Transmittance Spectra. The optical transmittance spectra are plotted in Figure 4. The transmittance spectra are similar to

that from nanostructured ZnO film.²⁶ Note that the interference oscillation period can not be found in the wide transparent region from the spectra. This is because the films are of the columnar growth formation with the diameter of about several tens nanometers and the surface rough layer of the film is thick. All the films are highly transparent in the visible region with an average transmission of 91%. As compared with the pure ZnO, the decrease of transmission illustrates that the materials become opaque as the TM doping, which is related to V_o and scattering at grain boundaries.¹⁶ This result is similar to that reported by Samanta et al. and Yadav et al.^{12,16} With further decreasing wavelength, a flat absorption edge appears in the region of 3.2–3.4 eV for all films due to the band to band transition. It indicates that there are Urbach tail states,²⁷ which can be attributed to crystalline defects and grain boundaries. In particular, the pure ZnO film has a most flat absorption edge near the band gap region. It suggests that there may be many defects in the film. The increasing of crystalline defects will decrease the diffraction intensity, which can be confirmed by the XRD results.

The excitonic features can also reflect the quality of the films, which is one of an important optical properties in ZnO materials. A distinct and strong peak can be observed in the strong absorption region due to excitonic optical transitions (see Figure 4). It suggests that the presence of the strong peak is a consequence of the large exciton binding energy.²⁸ The peak position of ZnO:TM films (about 344 nm) has a redshift of about 4 nm, as compared with that of undoped ZnO (about 340 nm). Hence, a larger Bohr radius will lead to a smaller oscillator strength, which indicates a weaker intensity of excitonic transitions.²⁸ Additionally, the intensity decreases with decreasing the OBG. Based on the effective mass approximation theory,^{10,29} the shift value ΔE_b from the bulk optical band gap is inversely proportional to the square of the grain size r for low-dimensional materials $\Delta E_b \propto (\hbar^2\pi^2)/(2m^*r^2)$. Here, m^* is the effective mass of the ZnO system. Thus, the shift value can be strikingly increased due to a smaller grain size of about 30 nm for the nc-ZnO:TM films, which results in the band gap shifts toward the high-energy side.

On the other hand, the OBG variation trend of the films can be distinguished from the absorption edges of transmittance spectra. As can be found from the inset of Figure 4, the decreasing order of OBG is ZnO, ZnO:Cr, ZnO:Mn, and ZnO:Ni film, respectively. It suggests that the OBG of the films decreases with increasing the orbital occupation numbers of 3d electrons. In nc-ZnO:TM films, the O ions around TM ions form an octahedral crystal field, splitting the 3d orbitals to a lower doublet e_g state and a higher-energy triplet t_{2g} state.³⁰ Because of the strongly hybridized with the p orbitals, the t_{2g} states further splitting into t_{bonding} and $t_{\text{antibonding}}$ states.⁸ The $t_{\text{antibonding}}$ states have higher energy and lie close to the conduction band (CB), which indicates the CB will be decreased. Therefore, the OBG of the films will be decreased and the carriers can be easily transported into CB.⁸ The 3d electrons number of ZnO:Ni film is larger than that of ZnO:Mn and ZnO:Cr films. The more 3d electrons number will splitting into more $t_{\text{antibonding}}$ states, which will further results in the shrinkage of OBG. Therefore, the changing trend of the nc-ZnO:TM films could be from the 3d orbital splitting.

PL Properties. PL spectra of the films are shown in Figure 5. A UV luminescence peak, which is originated from free excitonic emission, can be measured at about 3.20 eV. The value is less than that of arsenic (As)-doped ZnO films (3.22 eV).⁶ It can be found that the UV peak position slightly decreases with

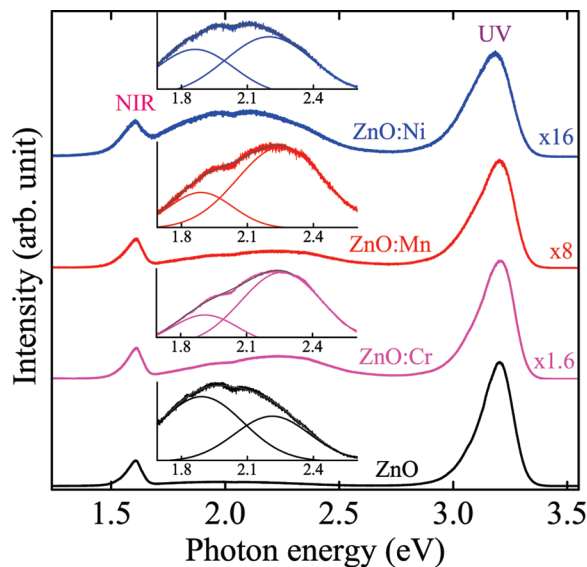


Figure 5. PL spectra of the undoped and ZnO:TM films at room temperature. The insets show the Gaussian model fitting results for the visible photon energy region from 1.7 to 2.6 eV. Two main emission bands (GL and RL) can be observed in the visible range.

the ionic radius of doping elements. The result can reflect the decreasing order of OBG, which is in good agreement with that observed by the transmittance spectra. Moreover, the UV PL emission intensity is strikingly decreased with the order of ZnO:Cr, ZnO:Mn, ZnO:Ni, and ZnO films. The quenching behavior of band gap luminescence was also observed in Mn- and Co-doped ZnO nanocrystals.¹⁴ As we know, TM doping can result in shallow donor and/or acceptor levels, which may be responsible for the variation trend of the present nc-ZnO:TM films, as discussed previously. Owing to the same experimental condition, the PL quantum efficiency of the undoped ZnO film can be found to be much higher than those of the nc-ZnO:TM materials. It could be ascribed to the magnetic element introductions and crystalline defects, which can degrade the recombination ability of the nonequilibrium carriers excited by the light.

On the other hand, the visible luminescences strongly depend on the doping elements. The decomposition of the visible band in the photon energy range from 1.7–2.6 eV by the Gaussian curve fitting reveals that it consists of green luminescence (GL) and red luminescence (RL). The RL is located at about 1.89, 1.91, 1.89, and 1.86 eV, respectively, while GL can be observed at about 2.21, 2.26, 2.25, and 2.20 eV, respectively. As compared with the pure ZnO film, the doping of TM can decrease the intensity of red peak while increase the intensity of green peak. Furthermore, the relatively integrated intensity (GL/RL) is 2.17, 1.92, and 1.24 for ZnO:Cr, ZnO:Mn, ZnO:Ni, respectively. It indicates that the defect centers for generating the two PL peaks are different and compete with each other from the magnetic ions. Many luminescence mechanisms have been proposed to interpret the origin of visible luminescences in ZnO semiconductor. A possible explanation is that the deep level defects V_o is responsible for the GL bands. The GL transition is from the recombination of a delocalized electron close to the CB with a deeply trapped hole in the single ionized V_o^+ centers.³¹ In addition, the green emission band could be attributed to the transition from the CB edge to the O interstitials (O_i) level formed in the band gap.³² The exact mechanism of the RLs located at about 1.90 eV is still controversial; intrinsic defects such as O_i might be considered as the origin.³³ Furthermore, different doping elements result in different

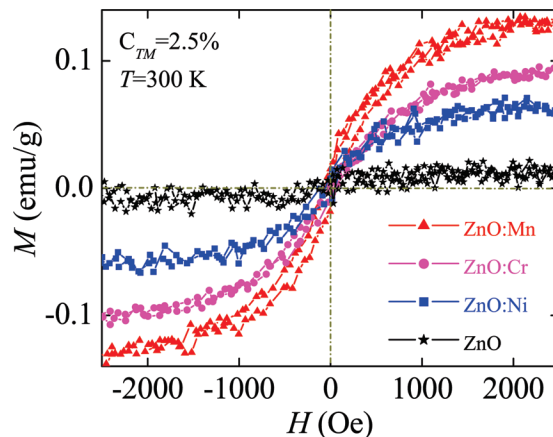


Figure 6. Room temperature magnetic hysteresis loops (MH curves) of the undoped and ZnO:TM nc films. Each curve was obtained by subtracting the diamagnetic contribution from the substrate.

morphologies, which can be confirmed by AFM results, and could affect the luminescence properties. For all films, a weak near-IR (NIR) peak can be determined at about 1.60 eV. This phenomenon could be ascribed to the second-order diffraction of the UV emission. It can be detected only in the film with a strong UV luminescence.³⁴ In order to further clarify the phenomena, the PL properties of the films at lower temperatures are necessary in the future work.

Magnetic Properties. It is widely recognized that the magnetic behavior of the ZnO:TM films strongly depend on the preparation conditions such as doping concentration, substrate temperature, and doping elements. Figure 6 presents the RT magnetization (M) vs magnetic field (H) curves of the undoped and nc-ZnO:TM films in the field range from -2500 to 2500 Oe. It can be found that all three nc-ZnO:TM films show the well-defined ferromagnetic features at RT. The coercivity is 34, 56, and 54 Oe for ZnO:Cr, ZnO:Mn, and ZnO:Ni film, respectively. These values are close to that found from 5% Co doped ZnO films (50 Oe)³⁵ while slightly less than that reported on 2.43% Mn doped ZnO hollow spherical structures (70 Oe).³⁶ Furthermore, the ZnO:Mn film exhibits a largest saturation magnetic moment (M_s) and the M_s of ZnO:Cr film is larger than that of ZnO:Ni film. Owing to a half-filled 3d band and relatively small ionic radius difference between Mn^{2+} and host cation Zn^{2+} , the Mn doping has a large magnetic moment properties.^{37,38} Hence, the ZnO:Mn film shows the largest M_s . The result is in good agreement with the previous theoretical prediction.^{1,39,40} The M_s is evaluated to be $0.335 \mu_B/Cr$, $0.512 \mu_B/Mn$, and $0.252 \mu_B/Ni$, respectively. The result is similar to that from ZnO:Cr samples prepared by the same method.⁴¹ Note that M_s of ZnO:Mn and ZnO:Ni films is slightly larger and smaller than that of previous reports, respectively.^{9,36,42} It can be attributed to the intrinsic defects such as V_o , O_i , and their distribution.¹ Furthermore, the different film structures could be another possible cause. Note further that these values are much smaller than that of the theoretic values, which can be commonly observed from DMS. This phenomenon can be ascribed to the antiferromagnetic superexchange interactions between adjacent TM ions, such as $Mn^{2+}-Mn^{2+}$ interactions.³⁶ Because of the antiferromagnetic competitions, ferromagnetic interactions are suppressed. Therefore, it will result in the M_s values much smaller than that calculated.⁴³ The results demonstrate a good magnetic performances of the present nc-ZnO:TM films. Finally, it can be also observed from Figure 6 that the undoped ZnO film exhibits a weak FM behavior. One even cannot recognize the coercivity and M_s of the sample due to

the unobvious magnetic signal. It suggests that the magnetic properties of ZnO:TM films mainly come from the doping of TM elements.

Up to date, it was widely believed that the magnetic properties of oxide materials are not exclusively related to the doping of magnetic ions but can be also determined by the defects, such as surface states, Zn_i , V_o , and O_i .^{1,14,44} It indicates that the defects play an certain role for the observed FM behavior of the nc-ZnO:TM materials. This conclusion can be confirmed by the weak FM property of undoped ZnO (see Figure 6). As discussed previously, the PL spectra, which can detect the interband and intraband transitions, can provide the information of defects in the nc-ZnO:TM films. From Figure 5, the emission intensity of the GL band is larger than that of the RL for the ZnO:TM films, as compared with the case in the undoped ZnO material, where an opposite trend can be observed. Theoretical predication suggests that filling vacancies will degrade the magnetic moment of the DMS materials, and the O_i has little effects on the magnetic moments.¹ Therefore, the present results confirm that the RL emission band is partly derived from the O_i . In addition, the quantities of V_o and O_i are remarkably different with the replacement of doping elements. The different structural defects will further affect the FM properties on the basis of the effects from TM dopants. It can be concluded that the defects of the nc-ZnO:TM films could be another cause for the observed magnetic properties. Moreover, the interfaces and grain boundaries could play an important role in enhancing the magnetic properties of the nc-ZnO:TM films.^{45,46} It was reported that FM behavior appears when the ratio of grain boundary area to grain volume exceeds a certain threshold.⁴⁷ The increase of domain volumes and the generation of defects at interfaces in the nc-ZnO:TM films may also contribute to the magnetic properties.⁴⁸ Taking into account that the doping of magnetic ions, intrinsic defects, interfaces, and grain boundaries, the FM properties at RT could be ascribed to the total contributions from the above factors in the present nc-ZnO:TM materials.

IV. Conclusion

In summary, the pure and nc-ZnO:TM ($C_{TM} = 2.5\%$) films are prepared on quartz substrates by the sol-gel technique. The A_1 (LO) phonon mode redshifts 4 cm^{-1} with the ionic radius of doping elements, and the E_2^{high} phonon mode varies about 7 cm^{-1} with different films. It was found that the doping elements significantly affect the OBG and excitonic transitions of the films. TM dopant dependence of electronic transitions has been investigated using PL spectra. Orange, yellow, and red luminescences can be measured from different films and the origin of these emissions has been discussed. Large coercivity and saturation magnetic moment can be observed from all nc-ZnO:TM films. The origin of ferromagnetic properties is discussed by spectral and magnetism experiments in detail. It can be concluded that the FM properties at RT could be induced from the total contributions due to the doping of magnetic ions, intrinsic defects, interfaces, and grain boundaries in the present nc-ZnO:TM materials. The present results are beneficial for the potential application of ZnO-based DMS optoelectronic devices.

Acknowledgment. This work was financially supported by Natural Science Foundation of China (Grant No. 60906046), Major State Basic Research Development Program of China (Grant No. 2007CB924901), Program of New Century Excellent Talents, MOE (Grant No. NCET-08-0192), Shanghai Municipal Commission of Science and Technology Project (Grant Nos. 10DJ1400201, 08JC1409000, 08520706100, and 09ZZ42), and the Fundamental Research Funds for the Central Universities.

References and Notes

- Wan, Q.; Sun, Q.; Jena, P.; Kawazoe, Y. *Phys. Rev. B* **2009**, *79*, 115407.
- Özgür, Ü.; Alivov, Ya. I.; Liu, C.; Teke, A.; Reshchikov, M. A.; Doğan, S.; Avrutin, V.; Cho, S. -J.; Morkoç, H. *J. Appl. Phys.* **2005**, *98*, 041301.
- Dietl, T.; Ohno, H.; Matsukura, F.; Cibert, J.; Ferrand, D. *Science* **2000**, *287*, 1019.
- Kim, K. J.; Park, Y. R. *Appl. Phys. Lett.* **2002**, *81*, 1420.
- Du, C. L.; Gu, Z. B.; You, Y. M.; Kasim, J.; Yu, T.; Shen, Z. X.; Ni, Z. H.; Ma, Y.; Cheng, G. X.; Chen, Y. F. *J. Appl. Phys.* **2008**, *103*, 023521.
- Li, W. W.; Hu, Z. G.; Wu, J. D.; Sun, J.; Zhu, M.; Zhu, Z. Q.; Chu, J. H. *J. Phys. Chem. C* **2009**, *113*, 18347.
- Liao, Z. M.; Zhang, H. Z.; Zhou, Y. B.; Xu, J.; Zhang, J. M.; Yu, D. P. *Phys. Lett. A* **2008**, *372*, 4505.
- Singh, S.; Rao, M. S. R. *Phys. Rev. B* **2009**, *80*, 045210.
- Yu, W.; Yang, L. H.; Teng, X. Y.; Zhang, J. C.; Zhang, Z. C.; Zhang, L.; Fu, G. S. *J. Appl. Phys.* **2008**, *103*, 093901.
- Hu, Z. G.; Li, Y. W.; Zhu, M.; Zhu, Z. Q.; Chu, J. H. *Phys. Lett. A* **2008**, *372*, 4521.
- Manivannan, A.; Dutta, P.; Glaspell, G.; Seehra, M. S. *J. Appl. Phys.* **2006**, *99*, 08M110.
- Samanta, K.; Bhattacharya, P.; Katiyar, R. S. *Appl. Phys. Lett.* **2005**, *87*, 101903.
- Panigrahy, B.; Aslam, M.; Misra, D. S.; Ghosh, M.; Bahadur, D. *Adv. Funct. Mater.* **2010**, *20*, 1161.
- Inamdar, D. Y.; Lad, A. D.; Pathak, A. K.; Dubenko, I.; Ali, N.; Mahamuni, S. *J. Phys. Chem. C* **2010**, *114*, 1451.
- Yu, W. L.; Li, W. W.; Wu, J. D.; Sun, J.; Zhu, J. J.; Zhu, M.; Hu, Z. G.; Chu, J. H. *J. Phys. Chem. C* **2010**, *114*, 8593.
- Yadav, H. K.; Sreenivas, K.; Gupta, V. *J. Appl. Phys.* **2006**, *99*, 083507.
- Mathew, X.; Enriquez, J. P.; García, C. M.; Contreras-Puente, G.; Cortes-Jacome, M. A.; Antonio, J. A. T.; Hays, J.; Punnoose, A. *J. Appl. Phys.* **2006**, *100*, 073907.
- Bai, L. Z.; Xing, Z. Z.; Sheng, X.; Su, F. H.; Li, G. H.; Wu, X. G. *Jpn. J. Appl. Phys.* **2008**, *47*, 2225.
- Ye, J. D.; Tripathy, S.; Ren, F. F.; Sun, X. W.; Lo, G. Q.; Teo, K. L. *Appl. Phys. Lett.* **2009**, *94*, 011913.
- Samanta, K.; Dussan, S.; Katiyar, R. S.; Bhattacharya, P. *Appl. Phys. Lett.* **2007**, *90*, 261903.
- Wang, H.; Chen, Y.; Wang, H. B.; Zhang, C.; Yang, F. J.; Duan, J. X.; Yang, C. P.; Xu, Y. M.; Zhou, M. J.; Li, Q. *Appl. Phys. Lett.* **2007**, *90*, 052505.
- Thakur, J. S.; Auner, G. W.; Naik, V. M.; Sudakar, C.; Kharel, P.; Lawes, G.; Suryanarayanan, R.; Naik, R. *J. Appl. Phys.* **2007**, *102*, 093904.
- Gao, K.; Zhang, W.; Sun, J.; Xu, N.; Ying, Z. F.; Li, Q.; Gan, J.; Wu, J. D. *J. Phys. Chem. C* **2009**, *113*, 19139.
- Artús, L.; Cuscó, R.; Ibáñez, J.; Blanco, N.; González-Díaz, G. *Phys. Rev. B* **1999**, *60*, 5456.
- Ashkenov, N.; Mbenkum, B. N.; Bundesmann, C.; Riede, V.; Lorenz, M.; Spemann, D.; Kaidashev, E. M.; Kasic, A.; Schubert, M.; Grundmann, M.; Wagner, G.; Neumann, H.; Darakchieva, V.; Arwin, H.; Monemar, B. *J. Appl. Phys.* **2003**, *93*, 126.
- Malandrino, G.; Blandino, M.; Fragala, M. E.; Losurdo, M.; Bruno, G. *J. Phys. Chem. C* **2008**, *112*, 9595.
- Urbach, F. *Phys. Rev.* **1953**, *92*, 1324.
- Tampo, H.; Shibata, H.; Maejima, K.; Yamada, A.; Matsubara, K.; Fons, P.; Niki, S.; Tainaka, T.; Chiba, Y.; Kanie, H. *Appl. Phys. Lett.* **2007**, *91*, 261907.
- Luttinger, J. M.; Kohn, W. *Phys. Rev.* **1955**, *97*, 869.
- Wang, X. L.; Dai, Z. X.; Zeng, Z. *J. Phys.: Condens. Matter* **2008**, *20*, 045214.
- Wu, X. L.; Siu, G. G.; Fu, C. L.; Ong, H. C. *Appl. Phys. Lett.* **2001**, *78*, 2285.
- Lin, Y. J.; Tsai, C. L.; Lu, Y. M.; Liu, C. J. *J. Appl. Phys.* **2006**, *99*, 093501.
- Wang, M. S.; Cheng, X. N.; Yang, J. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *96*, 783.
- Wang, Y. G.; Lau, S. P.; Lee, H. W.; Yu, S. F.; Tay, B. K.; Zhang, X. H.; Hng, H. H. *J. Appl. Phys.* **2003**, *94*, 354.
- Ueda, K.; Tabata, H.; Kawai, T. *Appl. Phys. Lett.* **2001**, *79*, 988.
- Lin, X. X.; Zhu, Y. F.; Shen, W. Z. *J. Phys. Chem. C* **2009**, *113*, 1812.
- Mandal, S. K.; Das, A. K.; Nath, T. K.; Karmaker, D. *Appl. Phys. Lett.* **2006**, *89*, 144105.
- Cong, C. J.; Liao, L.; Li, J. C.; Fan, L. X.; Zhang, K. L. *Nanotechnology* **2006**, *17*, 1520.
- Yun, S. Y.; Cha, G. B.; Kwon, Y.; Cho, S.; Hong, S. C. *J. Magn. Magn. Mater.* **2004**, *272*, e1563.
- Gopal, P.; Spaldin, N. A. *Phys. Rev. B* **2006**, *74*, 094418.

(41) Liu, H.; Zhang, X.; Li, L.; Wang, Y. X.; Gao, K. H.; Li, Z. Q.; Zheng, R. K.; Ringer, S. P.; Zhang, B.; Zhang, X. X. *Appl. Phys. Lett.* **2007**, *91*, 072511.

(42) Sharma, P.; Gupta, A.; Rao, K. V.; Owens, F. J.; Sharma, R.; Ahuja, R.; Guillen, J. M. O.; Johansson, B.; Gehring, G. A. *Nat. Mater.* **2003**, *2*, 673.

(43) Mi, W. B.; Bai, H. L.; Liu, H.; Sun, C. Q. *J. Appl. Phys.* **2007**, *101*, 023904.

(44) Liu, X. F.; Iqbal, J.; Wu, Z. B.; He, B.; Yu, R. H. *J. Phys. Chem. C* **2010**, *114*, 4790.

(45) Kittilstved, K. R.; Norberg, N. S.; Gamelin, D. R. *Phys. Rev. Lett.* **2005**, *94*, 147209.

(46) Schwartz, D. A.; Norberg, N. S.; Nguyen, Q. B.; Parker, J. M.; Gamelin, D. R. *J. Am. Chem. Soc.* **2003**, *125*, 13205.

(47) Straumal, B. B.; Mazilkin, A. A.; Protasova, S. G.; Myatiev, A. A.; Straumal, P. B.; Schütz, G.; Van Aken, P. A.; Goering, E.; Baretzky, B. *Phys. Rev. B* **2009**, *79*, 205206.

(48) Radovanovic, P. V.; Gamelin, D. R. *Phys. Rev. Lett.* **2003**, *91*, 157202.

JP103183V