Multiferroic ZnO obtained by substituting oxygen with nitrogen*

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N-doped ZnO films were prepared in nitrogen plasma by pulsed laser deposition. Clear room temperature ferromagnetism has been observed in the film prepared at a substrate temperature of 500 °C. The structural characterizations of X-ray diffraction, Raman, and X-ray photoelectron spectroscopy confirm the substitution of O by N in ZnO, which has been considered to be the origin of the observed ferromagnetism. Furthermore, ferroelectricity has been observed at room temperature by piezoelectric force microscopy, indicating the potential multiferroic applications.

Keywords: multiferroics, diluted magnetic semiconductor, ZnO

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1. Introduction

Multiferroic materials, exhibiting simultaneously the magnetic and ferroelectric order, have been widely studied in recent years due to their abundant physics and potential application in sensors, data storage, and spintronics.[1] ZnO is a direct wide band gap semiconductor ($E_g \sim 3.3$ eV at 300 K), which has wide applications in optical devices.[2] Ferroelectricity has been observed in ZnO with Zn site substitution by Li, Be, Mg, V, Cr, etc.[3−5] Especially for those 3d transition metals (V, Co, Cr, etc.) doped ZnO, the so-called diluted magnetic semiconductor (DMS),[6] room temperature ferromagnetism has also been reported.[7,8] Thus, ZnO might become a multiferroic DMS by appropriate ion doping.

Previously, to generate ferroelectricity and ferromagnetism, ions have been selected to dope mainly on the cation sites (Zn) in ZnO. No ferroelectricity has been reported on ZnO with ion doping on anion sites (O). Room-temperature ferromagnetism has also been observed in nonmagnetic ion-doped ZnO on anion sites; for example, C doping, where the ferromagnetic impurities can be excluded.[9,10] Theoretical calculation predicted possible ferromagnetism in oxides by substituting N for O.[11,12] However, experimentally, the incorporation of N into ZnO is difficult. In our previous study of the ZnO film prepared under a N_2 atmosphere, no N was detected.[13] In this paper, we report the preparation of ZnO film in N plasma, in which N has been clearly confirmed to substitute oxygen. Furthermore, room temperature ferromagnetism and ferroelectricity have been observed, indicating the potential multiferroic applications.

2. Experimental detail

N-doped ZnO films were prepared on surface-oxidized Si substrates by pulsed laser deposition (PLD) from pure ZnO (AR) targets. The base pressure was 5×10^{-5} Pa. During the film deposition and cooling, N plasma (N_2 pressure of 5 Pa) was applied. No voltage drop was applied directly onto the substrate. Two ZnO films were prepared at different substrate temperatures (T_s), ZnO-1 at T_s = 500 °C and ZnO-2 at T_s is room temperature. The film thickness of about 190 nm was controlled by the number of laser pulses (5000 in this paper) with pulse energy of 300 mJ and *ex-situ* determined by scanning elec-

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tron microscopy (SEM, FEI Quanta200). We used plastic tweezers and paid much attention to avoiding any contamination. The structures of the films were studied by X-ray diffraction (XRD, Rigaku UltimaIII) with Cu Kα radiation; Raman measurements (Horiba Jobin Yvon LabRAM HR 800) with a 785-nm excitation source; and X-ray photoelectron spectroscopy (XPS, ThermoFisher SCIENTIFIC) with an Al Kα X-ray source ($h\nu$ = 1486.6 eV). The ferroelectric behaviour was studied through piezoelectric force microscopy (PFM) with a scanning probe microscope (SPM, Veeco Nanoscope Dimension V). The magnetization was measured by a physical property measurement system (PPMS-9, Quantum Design).

3. Results and discussion

Figure 1 shows the XRD spectra. As can be clearly seen, only the ZnO (002) peak is observed for ZnO-1, indicating the highly (002) texture without any impurity phase. No diffraction peak can be observed for ZnO-2, indicating the amorphous structure. To clearly understand the doping effect of N, ZnO film under similar conditions as ZnO-1 without N plasma was prepared. The XRD pattern is shown in Fig. 1 (indicated by an arrow). It can be clearly seen that the (002) peak of ZnO-1 shift to higher angle, indicating the decrease of c lattice constant. The obvious shift of the (002) peak may be due to the fact that the length of the Zn–N bond is shorter than that of the Zn–O bond. This suggests the substitution of O mainly by N, instead of N_2.[14–16]

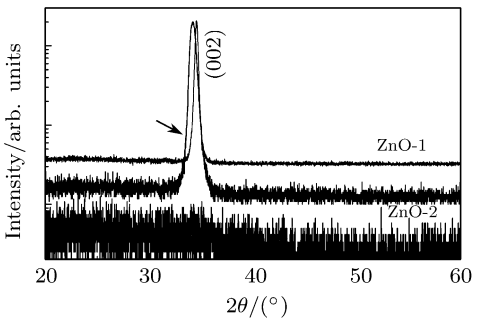


Fig. 1. The XRD patterns of ZnO-1 and ZnO-2. The arrow indicates the ZnO film prepared under similar conditions as ZnO-1 without N plasma.

Figure 2 shows the M–H curves for ZnO-1 and ZnO-2 measured at 300 K after subtracting the diamagnetic signal from the Si substrate and ZnO matrix. ZnO-1 exhibits a clear hysteresis loop, with saturation magnetization (M_s) of about 3 emu/cm^3. For ZnO-2, only negligible weak ferromagnetism can be observed. As the ZnO film prepared at T_s = 500 °C in 10 Pa O_2 only exhibits diamagnetism, the possibility of ferromagnetic impurities can be excluded.[17] To exclude the ferromagnetic contribution of O vacancies, the M–H curve of ZnO film under similar conditions as ZnO-1 without N plasma is presented (indicated by arrows). As can be seen, the magnetization of ZnO-1 is much larger. Thus the enhancement of the magnetization can be attributed to the inclusion of N.

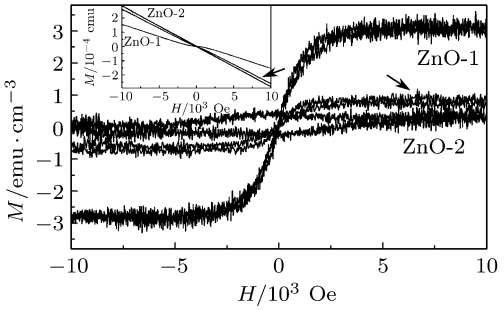


Fig. 2. The M–H curves for ZnO-1 and ZnO-2 after subtracting the high field linear background. The inset shows the raw data. The arrows indicate the ZnO film prepared under similar conditions as ZnO-1 without N plasma (1 Oe = 79.5775 A/m).

The hexagonal wurtzite ZnO belongs to the $P6_3mc$ space group and has the following optical modes: A_1+E_1+2E_2 (Raman active), 2B_1 modes (Raman silent), and A_1+E_1 modes (infrared active).[18] Figure 3 shows the room-temperature Raman spectrum of ZnO-1. Since the light penetration depth is larger than the thickness of the film, the modes of the Si substrate are also observed at 301 cm^{-1} and 521 cm^{-1}.[19] The peak at 437 cm^{-1} is commonly attributed to the E_2 (high) mode.[18] Besides the host phonons of ZnO, two peaks at 275 cm^{-1} and 578 cm^{-1} are observed and are considered to be N related.[20] The peak at 578 cm^{-1} can be ascribed to the formation of defects, such as oxygen vacancy (V_O), interstitial Zn (Zn_I), and lack of free carrier.[21] The peak at 275 cm^{-1} is attributed to the Zn_I–N_O complex, where N_O is the substitutional N at O sites.[22]

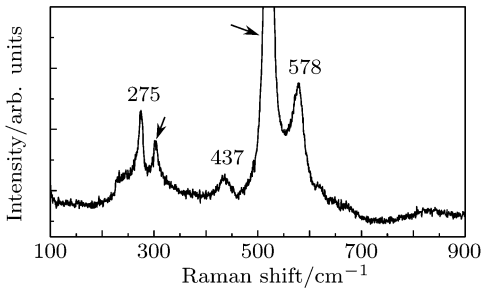


Fig. 3. Raman spectrum of ZnO-1. The arrows indicate the modes from the Si substrate.

Figure 4(a) shows the XPS survey spectrum of ZnO-1. Besides the C from the contaminations due to hydrocarbon adsorption on the sample surface from the laboratory environment, the spectrum contains all the major core lines of Zn and O, confirming the purity of the films.[23] Figure 4(b) shows the N1s XPS spectrum before (upper curve) and after (lower curve) etching the surface. The N1s spectrum can only be observed some depth below the surface, due to the fact that N cannot stay stable on the film surface.[24] The peak position determined by the fitting is 396.7 eV, which corresponds to the N substitution on O sites.[25]

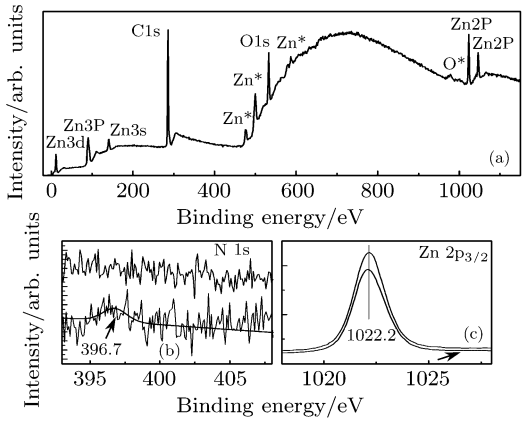


Fig. 4. (a) The XPS survey spectrum, (b) the XPS spectra of N1s, and (c) the XPS spectra of $Zn2P_{3/2}$ for ZnO-1. The upper curve in panel (b) was taken from the surface, and the bottom curve was taken after etching the surface. The arrow in panel (c) indicates the ZnO film prepared under similar conditions as ZnO-1 under 10 Pa O_2 and without N plasma.

In the present study, structural characterizations have clearly confirmed the N substitution on O sites, and the defect contribution to the observed ferromagnetism can be excluded, due to the much weaker ferromagnetism in the ZnO film with much higher defects concentration. Theoretical calculation has shown that local magnetic moments mainly located on N_O introduce a total moment of 1.0 μ_B/atom, and the long-range magnetic coupling can be attributed to a p–d exchange-like p–p coupling interaction involving holes.[26] Yu[27] suggested another possible mechanism that the net spin of one half can be induced in the d-orbit of Zn by electron transfer from Zn to N.[27] Figure 4(c) shows the $Zn2P_{3/2}$ spectrum of ZnO-1. For comparison, the $Zn2P_{3/2}$ spectrum of ZnO film prepared under similar conditions to ZnO-1 under 10 Pa O_2 without N plasma is also presented (indicated by the arrow). If there is electron transfer from Zn to N, the $Zn2P_{3/2}$ shift might be observed.[24] As can be seen in Fig. 4(c), both peaks are located at 1022.2 eV, indicating that no electron transfers from Zn to N. Thus the observed ferromagnetism can be concluded to be hole mediating between N_O. However, there is still a question about whether the hole concentration can be high enough to mediate this ferromagnetism, since the recent theoretical calculation points out that N is actually a deep acceptor.[28] The films are insulating, and the carrier type and concentration cannot be determined by the conventional Hall measurements. We suggest that the observed ferromagnetism might be explained by the bound magnetic polaron model.[29,30] The acceptor holes form the bound magnetic polarons, which overlap to create a spin-split impurity band to mediate the N_Os.

Figures 5(a) and 5(b) show the atomic force microscopy (AFM) and PFM images of ZnO-1, respectively. The domain pattern can be observed. Figure 5(c) shows the piezoelectric coefficient d_{33} versus the applied voltage hysteresis loop. Since the d_{33} in perovskite ferroelectrics can be expressed as $d_{33} = 2Q_{\rm eff}\varepsilon_0\varepsilon_{\rm r}P_{\rm s}$, where $Q_{\rm eff}$ is the effective electrostriction coefficient, $P_{\rm s}$, ε_0, and $\varepsilon_{\rm r}$ are spontaneous polarization, the permittivity of free space, and the relative permittivity, respectively.[4] The observed domain pattern and d_{33} loop indicate the ferroelectric behaviour of ZnO-1. The signal is weak, which might be due to the large leakage current because ZnO is a semiconductor.

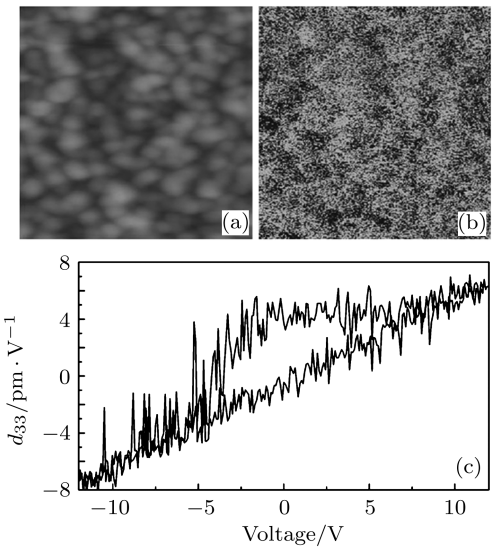


Fig. 5. (a) The AFM and (b) PFM images (1 μm × 1 μm), (c) the d_{33} versus applied voltage hysteresis loop of ZnO-1.

However, recent calculation points out that the ferroelectric behaviour might occur at a typical

semiconducting concentration of free carriers around 10^{17} cm^{-3}.[31] Thus it is suggested that better ferroelectric behaviour might be achieved by optimizing the film preparation. Our results clearly demonstrate ferroelectricity in ZnO due to ion substitution on anion sites (O). The mechanism of the ferroelectricity might be explained by the ionic radius difference (1.32 Å for N^{3-} and 1.24 Å for O^{2-}).[32] However, it must be noted that the mechanism for the ferroelectricity in ZnO is still an open question and needs further theoretical and experimental study.[33]

4. Conclusion

In conclusion, room-temperature ferromagnetism has been clearly observed in ZnO film prepared in N plasma by PLD at T_s of 500 °C. Structural characterization has confirmed the substitution of O by N. The ferromagnetism has been attributed to the hole mediating between N_O. Ferroelectricity due to the ionic radius difference between the doped and host anions has been observed. The observed ferromagnetism and ferroelectricity in N-doped ZnO indicate the potential multiferroic applications.

References

[1] Wang K F, Liu J M and Ren Z F 2009 *Adv. Phys.* **58** 321

[2] Özgür Ü, Alivov Ya I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S J and Morkoç H 2005 *J. Appl. Phys.* **98** 041301

[3] Onodera A 2002 *Ferroelectrics* **267** 131, and references therein

[4] Yang Y C, Song C, Wang X H, Zeng F and Pan F 2008 *J. Appl. Phys.* **103** 074107

[5] Yang Y C, Song C, Zeng F, Pan F, Xie Y N and Liu T 2007 *Appl. Phys. Lett.* **90** 242903

[6] Ohno H 1998 *Science* **281** 951

[7] Yang Y C, Zhong C F, Wang X H, He B, Wei S Q, Zeng F and Pan F 2008 *J. Appl. Phys.* **104** 064102

[8] Lin Y, Ying M, Li M, Wang X and Nan C 2007 *Appl. Phys. Lett.* **90** 222110

[9] Zhou S, Xu Q, Potzger K, Talut G, Grötzsche R, Fassbender J, Vinnichenko M, Grenzer J, Helm M, Hochmuth H, Lorenz M, Grundmann M and Schmidt H 2008 *Appl. Phys. Lett.* **93** 232507

[10] Pan H, Yi J B, Shen L, Wu R Q, Yang J H, Lin J Y, Feng Y P, Ding J, Van L H and Yin J H 2007 *Phys. Rev. Lett.* **99** 127201

[11] Elfimov I S, Rusydi A, Csiszar S I, Hu Z, Hsieh H H, Lin H J, Chen C T, Liang R and Sawatzky G A 2007 *Phys. Rev. Lett.* **98** 137202

[12] Shi L, Jin J and Zhang T 2010 *Chin. Phys.* B **19** 127001

[13] Xu Q, Schmidt H, Zhou S, Potzger K, Helm M, Hochmuth H, Lorenz M, Setzer A, Esquinazi P, Meinecke C and Grundmann M 2008 *Appl. Phys. Lett.* **92** 082508

[14] Li L, Shan C X, Li B H, Zhang J Y, Yao B, Shen D Z, Fan X W and Lu Y M 2010 *J. Mater. Sci.* **45** 4093

[15] Barnes T M, Olson K and Wolden C A 2005 *Appl. Phys. Lett.* **86** 112112

[16] Yao B, Shen D Z, Zhang Z Z, Wang X H, Wei Z P, Li B H, Lü Y M, Fan X W, Guan L X, Xing G Z, Cong C X and Xie Y P 2006 *J. Appl. Phys.* **99** 123510

[17] Xu Q, Wen Z, Xu L, Gao J, Wu D, Shen K, Qiu T, Tang S and Xu M 2011 *Physica* B **406** 19

[18] Agarwal D C, Singh F, Kabiraj D, Sen S, Kulariya P K, Sulania I, Nozaki S, Chauhan R S and Avasthi D K 2008 *J. Phys.* D: *Appl. Phys.* **41** 045305, and references therein

[19] Xiao Z, Liu Y, Zhang J, Zhao D, Lu Y, Shen D and Fan X 2005 *Semicond. Sci. Technol.* **20** 796

[20] Kaschner A, Haboeck U, Strassburg M, Strassburg M, Kaczmarczyk G, Hoffmann A, Thomsen C, Zeuner A, Alves H R, Hofmann D M and Meyer B K 2002 *Appl. Phys. Lett.* **80** 1909

[21] Sui Y R, Yao B, Yang J H, Cui H F, Huang X M, Yang T, Gao L L, Deng R and Shen D Z 2010 *Appl. Surf. Sci.* **256** 2726

[22] Friedrich F, Gluba M A and Nickel N H 2009 *Appl. Phys. Lett.* **95** 141903

[23] Wei L, Li Z and Zhang W F 2009 *Appl. Surf. Sci.* **255** 4992

[24] Cao P, Zhao D X, Zhang J Y, Shen D Z, Lu Y M, Yao B, Liu B H, Bai Y and Fan X W 2008 *Appl. Surf. Sci.* **254** 2900

[25] Perkins C L, Lee S, Li X, Asher S E and Coutts T J 2005 *J. Appl. Phys.* **97** 034907

[26] Shen L, Wu R Q, Pan H, Peng G W, Yang M, Sha Z D and Feng Y P 2008 *Phys. Rev.* B **78** 073306

[27] Yu C, Lin T, Sun S and Chou H 2007 *J. Phys.* D: *Appl. Phys.* **40** 6497

[28] Lyons J L, Janotti A and van der Walle C G 2009 *Appl. Phys. Lett.* **95** 252105

[29] Coey J M D, Venkatesan M and Fitzgerald C B 2005 *Nature Mater.* **4** 173

[30] Zou C W, Wang H J, Yi M L, Li M, Liu C S, Guo L P, Fu D J and Kang T W 2010 *Appl. Surf. Sci.* **256** 2453

[31] Glinchuk M D, Kirichenko E V, Stephanovich V A and Zaulychny B Y 2009 *J. Appl. Phys.* **105** 104101

[32] Shannon R D 1976 *Acta Cryst.* A **32** 751

[33] Tagantsev A K 2008 *Appl. Phys. Lett.* **93** 202905