

# Room Temperature Multiferroicity in $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ Film Prepared in N Plasma

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**Abstract**  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  films have been prepared under different conditions by pulsed laser deposition. Ferromagnetism with saturate magnetization of about  $7 \text{ emu/cm}^3$  at 300 K has been observed in  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film prepared in N plasma at room temperature. The concentration of oxygen vacancies was increased by N substituting O in N plasma, and the ferromagnetism originated from the aligned magnetic moments of more Cu ions mediated by oxygen vacancies. Furthermore, ferroelectricity has been confirmed by the observation of the electrical field dependent converse piezoelectric coefficient  $d_{33}$  loop at room temperature, indicating the potential multiferroic applications.

**Keywords** ZnO · Multiferroicity · Diluted magnetic semiconductor · Ferromagnetism · Ferroelectricity

## 1 Introduction

Multiferroic materials possessing two or more kinds of ferroicities, such as ferromagnetism, ferroelectricity, ferroelasticity, and ferrotoroidicity, have attracted much attention [1]. However, the single phase multiferroic material is very rare

due to the mutual exclusion of the ferromagnetism and ferroelectricity [2]. Until now,  $\text{BiFeO}_3$  is the only multiferroic material with magnetic ordering (antiferromagnetism) and ferroelectricity both above room temperature (RT) [3]. Thus, much work has been done to search for the RT multiferroic materials.

ZnO has been predicted to be potential candidate for the diluted magnetic semiconductor (DMS) by proper magnetic ion substitution [4]. However, the mechanism for the observed weak ferromagnetism in ZnO-based DMS is still under debate. Recently, the observation of both weak ferromagnetism and ferroelectricity in Li and/or Co-doped ZnO indicates that ZnO might be a potential multiferroic material by suitable ion substitution [5]. In this paper, we prepared the  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film in N plasma at substrate temperature ( $T_s$ ) of RT; clear ferromagnetism and ferroelectricity were both observed at RT, indicating the potential multiferroic applications.

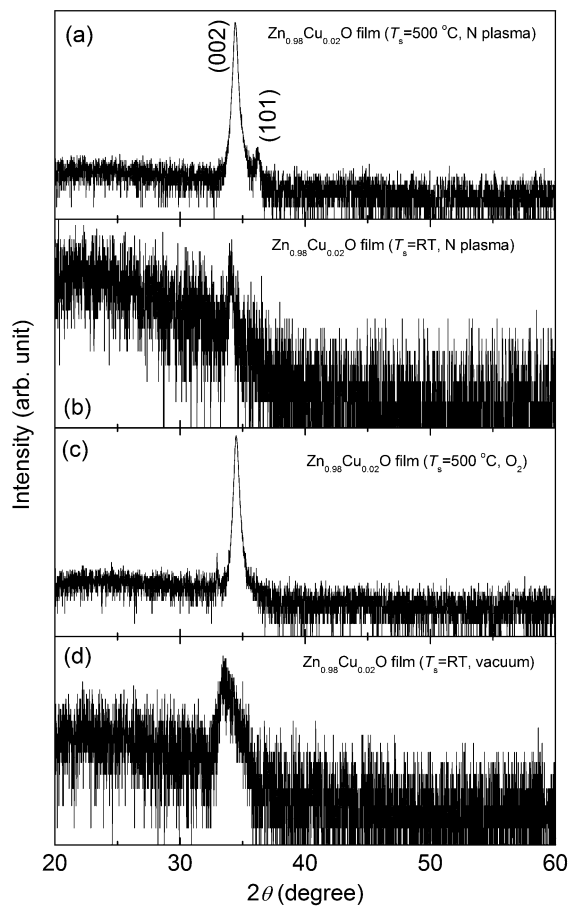
## 2 Experimental Details

$\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  films were prepared on surface oxidized Si substrates by pulsed laser deposition (PLD) with  $T_s$  of RT or  $500^\circ\text{C}$ , and in N plasma ( $\text{N}_2$  pressure of 5 Pa), vacuum, or  $\text{O}_2$  atmosphere (5 Pa). The base pressure of the chamber is  $5 \times 10^{-5}$  Pa. The thickness of the films was controlled by the laser pulse number, and ex situ determined to be about 130 nm. We used plastic tweezers and paid much attention to avoid any contamination. The structure of the films was studied by X-ray diffraction (XRD, Rigaku UltimaIII) with Cu  $K\alpha$  radiation, and X-ray photoelectron spectroscopy (XPS, ThermoFisher SCIENTIFIC) with Al  $K\alpha$  X-ray source ( $h\nu = 1486.6 \text{ eV}$ ). The magnetization was measured by a physical property measurement system (PPMS-9, Quantum Design). The ferroelectric behavior

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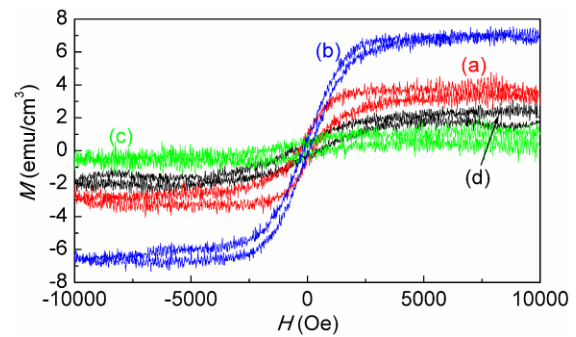


**Fig. 1** XRD patterns of  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  films (a) ( $T_s = 500^\circ\text{C}$ , N plasma), (b) ( $T_s = \text{RT}$ , N plasma), (c) ( $T_s = 500^\circ\text{C}$ ,  $\text{O}_2$ ), and (d) ( $T_s = \text{RT}$ , vacuum), the intensity is on the logarithmic scale

was studied through piezoelectric force microscopy (PFM) in a scanning probe microscope (SPM, Veeco Nanoscope Dimension V). X-ray absorption fine structure spectroscopy (XAFS) measurements were performed at the National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China (USTC). The energy range of the monochromatized X-rays was 4–13.5 KeV provided by a double crystal monochromator using Si(111).

### 3 Results and Discussion

Figure 1 shows the XRD patterns of  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  films prepared under different conditions. All the films exhibit only (002) diffraction peak, except for the  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film ( $T_s = 500^\circ\text{C}$ , N plasma) where a weak peak of (101) can be observed, indicating the highly (002) texture on the surface oxidized Si substrates without any impurity phases. The substrate temperature has significant influence on the crystalline quality. As can be seen from Fig. 1, the films prepared at  $500^\circ\text{C}$  shows sharp (002) peak, while the films prepared at RT show negligible weak (002) peak, indicating the

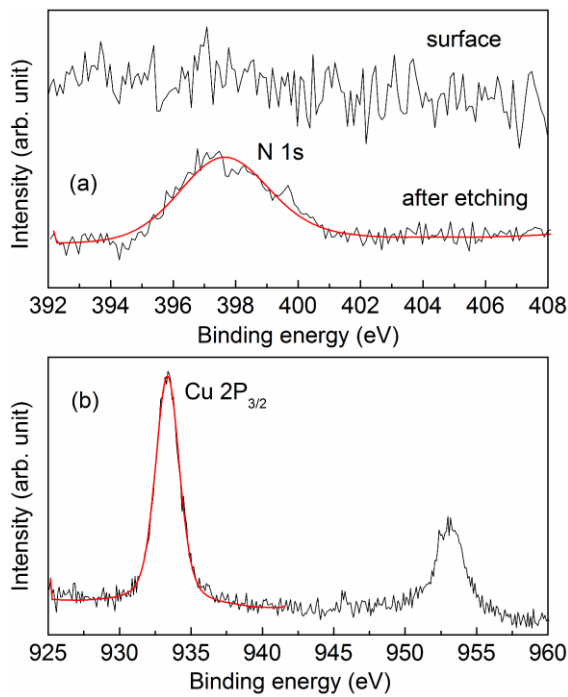


**Fig. 2**  $M$ – $H$  curves measured at 300 K for  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  films (a) ( $T_s = 500^\circ\text{C}$ , N plasma), (b) ( $T_s = \text{RT}$ , N plasma), (c) ( $T_s = 500^\circ\text{C}$ ,  $\text{O}_2$ ), and (d) ( $T_s = \text{RT}$ , vacuum)

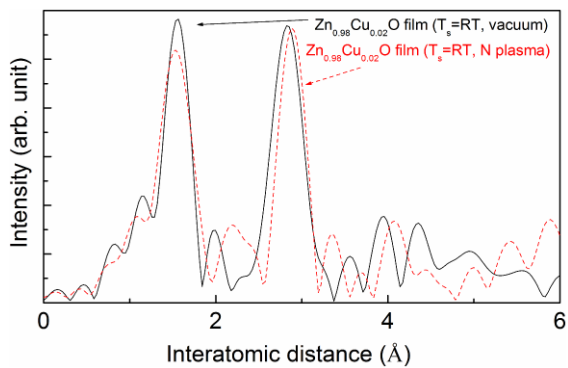
nearly amorphous structure of  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film ( $T_s = \text{RT}$ , N plasma).

Figure 2 shows the  $M$ – $H$  curves of  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  films after subtracting the high field diamagnetic signal. Weak ferromagnetism has been observed for all the films. However, for  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film ( $T_s = 500^\circ\text{C}$ ,  $\text{O}_2$ ), the saturate magnetization ( $M_s$ ) is negligible small, only about  $0.5 \text{ emu/cm}^3$ .  $M_s$  is about  $2 \text{ emu/cm}^3$  for  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film ( $T_s = \text{RT}$ , vacuum), and  $3.5 \text{ emu/cm}^3$  for  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film ( $T_s = 500^\circ\text{C}$ , N plasma) and  $7 \text{ emu/cm}^3$  for  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film ( $T_s = \text{RT}$ , N plasma). Since the defects in pure ZnO and N substituting O ( $\text{N}_\text{O}$ ) might also have ferromagnetic contributions [6–8], to explore the role of doping ions, we should compare the  $M_s$  with and without Cu doping under similar conditions. In pure ZnO film prepared in high vacuum at  $T_s$  of RT,  $M_s$  is about  $3.5 \text{ emu/cm}^3$  [9], and in N plasma at  $T_s$  of  $500^\circ\text{C}$ ,  $M_s$  is about  $3 \text{ emu/cm}^3$ , while in N plasma at  $T_s$  of RT  $M_s$  is only about  $0.2 \text{ emu/cm}^3$  [10]. This indicates the significant enhancement of the ferromagnetism with Cu substitution in ZnO prepared in N plasma at  $T_s$  of RT. Thus, in the following, we will concentrate on the  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film ( $T_s = \text{RT}$ , N plasma).

The XPS spectra were calibrated by taking the C 1s peak (284.8 eV) [11]. Figure 3(a) shows the N 1s spectrum for  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film ( $T_s = \text{RT}$ , N plasma). As can be seen, no peak can be observed at the film surface. After etching the film surface by  $\text{Ar}^+$  ion sputtering, a clear peak can be observed. This is due to that N cannot stay stable on the film surface [12]. Maki has confirmed the energy position of N substituting O site to be 398 eV, which is also very close to the energy position of N 1s in GaN [13]. The peak position determined by the fitting is 397.6 eV, which can be attributed to the N substitution on O sites and might be in valence state of  $-3$ . Figure 3(b) shows the Cu  $2\text{P}_{3/2}$  spectrum.  $2\text{P}_{3/2}$  peaks of  $\text{Cu}^+$  appear at 932.7 eV, and that of  $\text{Cu}^{2+}$  appears at 933.6 eV [14]. The peak position by fitting the spectrum is 933.4 eV, which suggests that the Cu ions are in a mixed state of  $+1$  and  $+2$ .

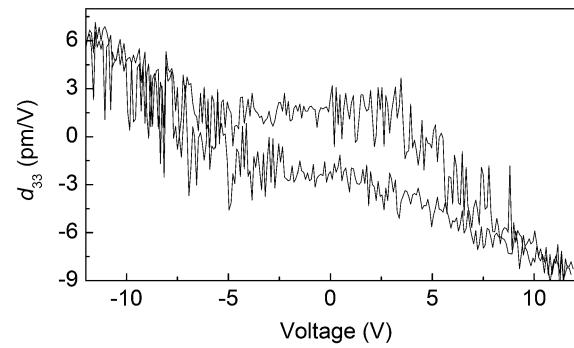


**Fig. 3** (a) N 1s spectrum taken at surface and after etching the surface by Ar<sup>+</sup>, and (b) Cu 2P<sub>3/2</sub> spectrum for Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , N plasma). The thick red curves are the fitting curves



**Fig. 4** Fourier transformed magnitude of XAFS spectra of Zn<sub>0.98</sub>Cu<sub>0.02</sub>O films ( $T_s = RT$ , N plasma) (dashed curve) and ( $T_s = RT$ , vacuum) (solid curve)

To further study the correlation of structure and magnetism of the Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film, XAFS spectra on Zn K edge were collected for Zn<sub>0.98</sub>Cu<sub>0.02</sub>O films ( $T_s = RT$ , N plasma) and ( $T_s = RT$ , vacuum). The detailed analysis will be published elsewhere. Figure 4 shows the corresponding Fourier transformed amplitude of XAFS spectra. Note that the first (~1.5 Å) and second (~2.85 Å) major peaks at the Zn K edge correspond to the first Zn–O (or N) shell and the second Zn–Zn (or Cu) shell, respectively [15]. As can be clearly seen, the first major peak is obviously broadened in Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , N plasma), indicating that the disorder is increased in film prepared in N



**Fig. 5** The  $d_{33}$  vs. applied voltage hysteresis loop of Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , N plasma)

plasma. The peak position moves to lower distance slightly (1.53 Å in Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , N plasma), 1.56 Å in Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , vacuum)). This may be caused by the increased concentration of O vacancies [15]. With the substitution of O by N, the more O vacancies can be tolerated by considering the charge balance since N in valence state of –3. The peak position of second major peak moves to larger distance slightly, indicating that the distance between Zn and the nearest Zn (or Cu) is larger in Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , N plasma). With higher concentration of O vacancies, the repulsion between the nearest neighboring cations will push them farther away from each other. Thus, the XAFS results confirm the substitution of O by N, and the higher concentration of O vacancies in Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , N plasma).

Based on above structural results, we can explain the enhanced ferromagnetism in Zn<sub>0.98</sub>Cu<sub>0.02</sub>O films ( $T_s = RT$ , N plasma) by the indirect double-exchange model suggested by Herg [16]. The Cu ions close to O vacancies will receive the electrons and behave more like  $d^{10}$  (Cu<sup>1+</sup>-like), with a mixture of  $d^9$  (Cu<sup>2+</sup>). The magnetic moments of neighboring Cu ions are aligned by the mediation of oxygen vacancies in the vicinity. In Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , N plasma), the concentration of O vacancies further increases with the substitution of O by N, thus more Cu ions can be mediated by oxygen vacancies, leading to the enhancement of ferromagnetism.

Figure 5 shows the converse piezoelectric coefficient  $d_{33}$  versus applied voltage hysteresis loop by randomly selecting a point on the film surface. The  $d_{33}$  in perovskite ferroelectrics can be expressed as:  $d_{33} = 2Q_{\text{eff}}\epsilon_0\epsilon_r P_s$ , where  $Q_{\text{eff}}$  is the effective electrostriction coefficient,  $P_s$ ,  $\epsilon_0$ , and  $\epsilon_r$  are spontaneous polarization, the permittivity of free space, and relative permittivity, respectively [17]. The observed  $d_{33}$  loop indicates the ferroelectric behavior of Zn<sub>0.98</sub>Cu<sub>0.02</sub>O film ( $T_s = RT$ , N plasma). Though the intrinsic nature of the ferroelectricity in doped ZnO is still under debate [18], it can be generally explained by the ionic radii difference between Zn<sup>2+</sup> (0.74 Å) and Cu<sup>1+</sup> (0.77 Å) or Cu<sup>2+</sup> (0.73 Å) [5, 19].

## 4 Conclusions

In summary, ferromagnetism with saturate magnetization of about  $7 \text{ emu/cm}^3$  at 300 K has been observed in  $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$  film prepared in N plasma at room temperature by PLD. The Cu has been determined to be in mixed valence state of +1 and +2, while N has been confirmed to substitute O in valence state of  $-3$ . The substitution of O by N further increases the concentration of O vacancies, which mediate more neighboring Cu ions, leading to the enhanced ferromagnetism. Furthermore, ferroelectricity was confirmed by the observation of the electrical field dependent piezoelectric coefficient  $d_{33}$  loop at room temperature, indicating the potential multiferroic applications.

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## References

1. Wang, K.F., Liu, J.-M., Ren, Z.F.: *Adv. Phys.* **58**, 321 (2009)
2. Khomskii, D.I.: *J. Magn. Magn. Mater.* **306**, 1 (2006)
3. Catalan, G., Scott, J.F.: *Adv. Mater.* **21**, 2463 (2009)
4. Dietl, T., Ohno, H., Matsukura, F., Cibert, J., Ferrand, D.: *Science* **287**, 1019 (2000)
5. Lin, Y., Ying, M., Li, M., Wang, X., Nan, C.: *Appl. Phys. Lett.* **90**, 222110 (2007)
6. Xu, Q., Schmidt, H., Zhou, S., Potzger, K., Helm, M., Hochmuth, H., Lorenz, M., Setzer, A., Esquinazi, P., Meinecke, C., Grundmann, M.: *Appl. Phys. Lett.* **92**, 082508 (2008)
7. Hong, N.H., Sakai, J., Brizé, V.: *J. Phys., Condens. Matter.* **19**, 036219 (2007)
8. Shen, L., Wu, R.Q., Pan, H., Peng, G.W., Yang, M., Sha, Z.D., Feng, Y.P.: *Phys. Rev. B* **78**, 073306 (2008)
9. Xu, Q., Wen, Z., Xu, L., Gao, J., Wu, D., Shen, K., Qiu, T., Tang, S., Xu, M.: *Physica B* **406**, 19 (2011)
10. Xu, Q.: unpublished
11. Wei, L., Li, Z., Zhang, W.F.: *Appl. Surf. Sci.* **255**, 4992 (2009)
12. Cao, P., Zhao, D.X., Zhang, J.Y., Shen, D.Z., Lu, Y.M., Yao, B., Liu, B.H., Bai, Y., Fan, X.W.: *Appl. Surf. Sci.* **254**, 2900 (2008)
13. Maki, H., Sakaguchi, I., Ohashi, N., Sekiguchi, S., Haneda, H., Tanaka, J., Ichinose, N.: *Jpn. J. Appl. Phys.* **42**, 75 (2003)
14. Ran, F., Tanemura, M., Hayashi, Y., Hihara, T.: *J. Cryst. Growth* **311**, 4270 (2009)
15. Liu, X., Shi, E., Chen, Z., Chen, B., Huang, W., Song, L., Zhou, K., Cui, M., Xie, Z., He, B., Wei, S.: *J. Alloys Compd.* **463**, 435 (2008)
16. Herng, T.S., Qi, D.-C., Berlijn, T., Yi, J.B., Yang, K.S., Dai, Y., Feng, Y.P., Santoso, I., Sánchez-Hanke, C., Gao, X.Y., Wee, A.T.S., Ku, W., Ding, J., Rusydi, A.: *Phys. Rev. Lett.* **105**, 207201 (2010)
17. Yang, Y.C., Song, C., Wang, X.H., Zeng, F., Pan, F.: *J. Appl. Phys.* **103**, 074107 (2008)
18. Tagantsev, A.K.: *Appl. Phys. Lett.* **93**, 202905 (2008)
19. Shannon, R.D.: *Acta Crystallogr. A, Found. Crystallogr.* **32**, 751 (1976)