

Z.H. SUN
Y.L. ZHOU✉
S.Y. DAI
L.Z. CAO
Z.H. CHEN

Preparation and properties of GaFeO₃ thin films grown at various oxygen pressures by pulsed laser deposition

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, P.R. China

Received: 3 July 2007 / Accepted: 9 November 2007
Published online: 19 December 2007 • © Springer-Verlag 2007

ABSTRACT GaFeO₃ thin films were prepared on (111)-oriented SrTiO₃:Nb substrates under various oxygen pressures from 0.1 to 10 Pa at 700 °C by using a pulsed laser deposition method. Effects of the oxygen pressures on the crystallinity, dielectric and ferroelectric properties of the thin films were investigated at room temperature. The results show that the GaFeO₃ thin films exhibit ferroelectricity and the properties of the thin films are influenced markedly by the deposition oxygen pressures.

PACS 68.55.Jk; 77.55.+f; 77.22.Ej

1 Introduction

Multiferroics are a kind of novel functional materials. Ferromagnetic and ferroelectric orders coexist in these materials and their physical behaviors can be modulated by a magnetic and/or electric field, respectively [1]. The coupling between the two order parameters can lead to a series of new phenomena and potential applications, such as magnetodielectric and magneto-electric effects, etc., which could be used in some novel devices [2, 3]. In recent years, multiferroics have incurred great interest and have been investigated extensively. Ga_{2-x}Fe_xO₃ oxides have been proved to be a promising candidate for potential application [4–6]. The structure and physical properties, such as magneto-electric properties, magneto-optical properties and the optical magneto-electric effect, etc., of the single-crystal samples have been extensively studied, but the properties of the thin films of this material are rarely reported so far. However, the device integration and application requires exploring the techniques of the preparation of the crystalline thin films on different substrates. On the GaFeO₃ (GFO) thin film, that is not easily prepared due to the orthorhombic structure of the crystal lattice, Kundaliya et al. have reported a study of the large second-harmonic Kerr rotation recently [7], but other properties, such as dielectric, ferroelectric, magnetic and op-

tical properties, etc., have not been reported for the thin film until now.

In this work, we have prepared GaFeO₃ thin films on the (111) plane of SrTiO₃:Nb (STON) substrates by pulsed laser deposition (PLD) and the dielectric and ferroelectric properties of the thin films have been investigated. This study is focused on the effect of deposition oxygen pressure on the crystallization, leakage current and dielectric and ferroelectric properties at room temperature (RT).

2 Experimental

Pulsed laser deposition equipment was employed to prepare GaFeO₃ thin films under various oxygen pressures of 10 Pa, 1 Pa and 0.1 Pa. The detailed deposition conditions are listed in Table 1. The thickness of the thin films was measured using scanning electron microscopy (SEM). Crystalline structures of the thin films were checked by X-ray diffraction (XRD, Rigaku). Atomic force microscopy (AFM) was used to characterize the root mean square (RMS) roughness of the thin films.

To form a parallel-plate capacitor structure for measuring the dielectric and ferroelectric properties, the conductive STON substrates acted as the bottom electrode, and some platinum (Pt) dots with 100-nm thickness deposited at room temperature under high vacuum (5×10^{-3} Pa) served as the top electrode. In addition, to obtain a good contact between the film and the Pt electrode, a rapid thermal post-annealing (RTP) was taken in the atmosphere at 400 °C for 6 min. Dielectric measurements of the GaFeO₃ thin films were carried out on an Agilent 4294A precision impedance analyzer and

Target	GaFeO ₃ ceramic disk
Substrate	(111)-oriented STON
Substrate temperature	700 °C
Gas pressure (O ₂)	0.1–10 Pa
Laser	XeCl excimer ($\lambda = 308$ nm)
Repetition frequency	3 Hz
Target–substrate distance	45 mm
Deposition time	30 min

TABLE 1 Deposition conditions of the GaFeO₃ thin films by PLD

✉ Fax: +86-10-82649531, E-mail: ylzhou@aphy.iphy.ac.cn

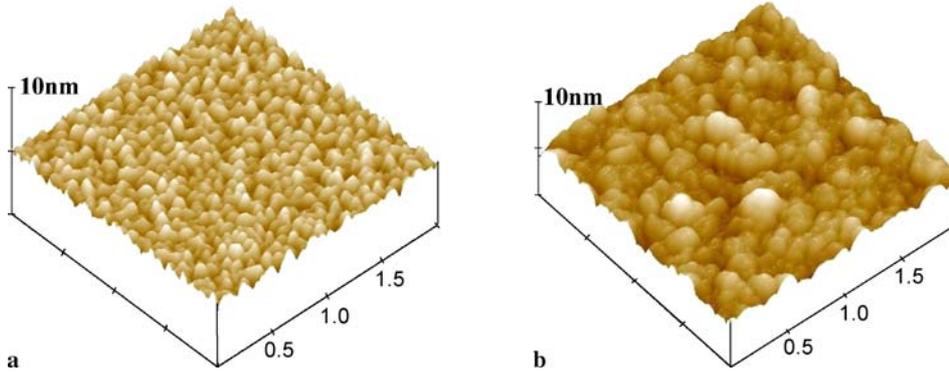


FIGURE 2 AFM images of the GaFeO₃ thin films deposited at (a) 10 Pa and (b) 0.1 Pa, respectively

ferroelectric loops were measured using a RT6000 ferroelectric analyzer at room temperature.

3 Results and discussion

The effect of oxygen pressures on the crystalline phase and structure of the GFO thin films was identified by the XRD analysis. Figure 1 shows the θ - 2θ scans of the GFO thin films deposited at various oxygen pressures. As revealed from Fig. 1, oriented (0/0) GaFeO₃ thin films were obtained when the oxygen pressure was held at about 10 Pa, whereas obvious extra peaks belonging to other orientations of GaFeO₃ bulk samples were observed in the thin films deposited at other oxygen pressures. This could be attributed to the large lattice mismatch between GFO and STON substrates. Generally, GaFeO₃ crystallizes in the orthorhombic structure with lattice constants of $a = 8.747 \text{ \AA}$, $b = 9.394 \text{ \AA}$ and $c = 5.082 \text{ \AA}$ [8], and it may also show the pseudo-hexagonal crystal structure with $a' = 10.116 \text{ \AA}$ and $c' = 9.394 \text{ \AA}$ in single-crystal growth [9]. While the (111)-oriented STON substrates have the hexagonal plane with lattice parameters about 11.02 \AA , the in-plane lattice mismatch between GFO and STON is about 8.2%. The large lattice mismatch brings a difficulty in depositing good oriented thin films. Therefore, only under due deposition conditions can oriented thin films be obtained. Thus, this could be used to interpret the XRD results here. We should note that the (0/0) orientations labeled

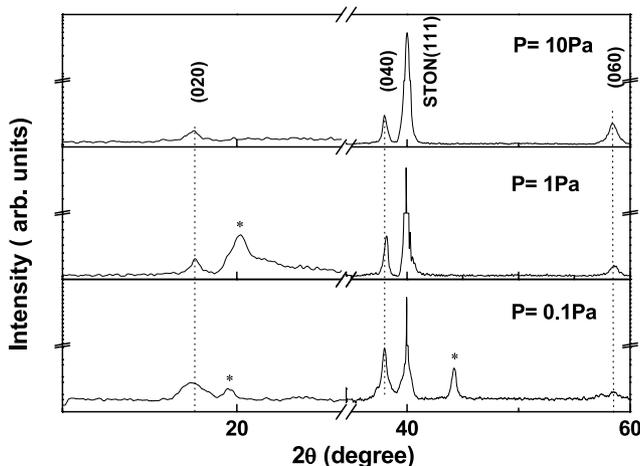


FIGURE 1 XRD patterns of the GaFeO₃ thin films

in Fig. 1 are the original indices of the orthorhombic structure. Figure 2 shows the AFM images of the GaFeO₃ thin films. The surface RMS roughness of the thin films deposited at 10 Pa and 0.1 Pa is about 2 nm and 4 nm, respectively, which means that the oxygen pressure has affected the crystallization of GaFeO₃ thin films.

The leakage current of the thin films as a function of applied electric field is comparably shown in Fig. 3. It is observed that the deposition oxygen pressure does influence the

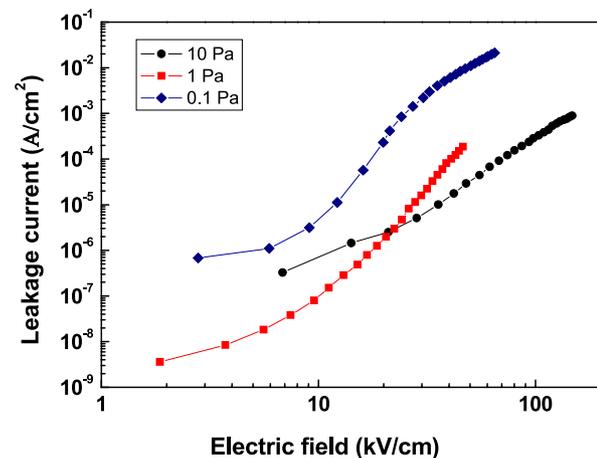


FIGURE 3 Leakage current of the thin films deposited under different oxygen pressures

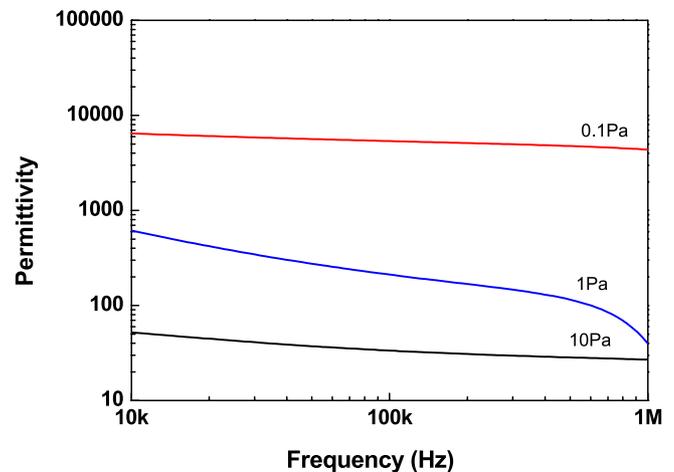


FIGURE 4 Dielectric properties of the GaFeO₃ thin films

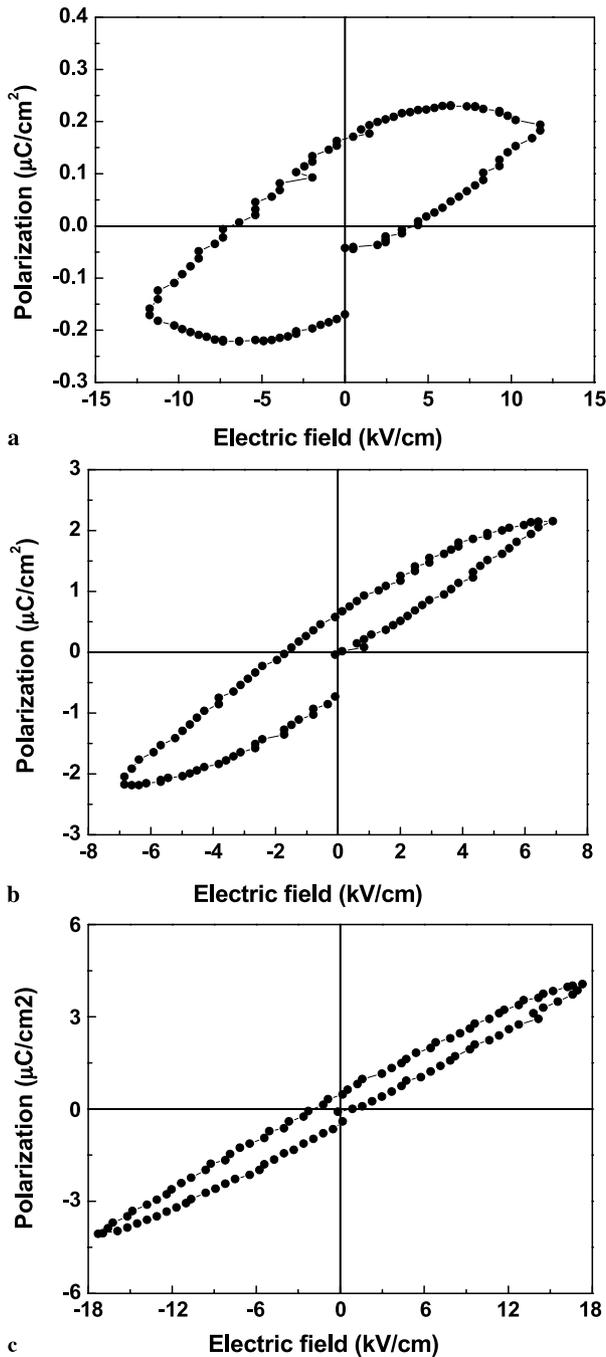


FIGURE 5 Ferroelectric loops of the GaFeO₃ thin films grown at (a) 10 Pa, (b) 1 Pa and (c) 0.1 Pa

leakage current. As the electric field rises over 20 kV/cm, the leakage current evidently increases with the decrease of oxygen pressure. According to the reported results for BiFeO₃ thin films [10, 11], we think that the decrease of leakage current of the GaFeO₃ thin films with the deposition oxygen pressure is related to the oxygen vacancies in the films.

The dielectric constant of the GFO thin films as a function of measuring frequency (10^4 – 10^6 Hz) is shown in Fig. 4. It is observed that the permittivity increases on decreasing the deposition oxygen pressure. At a frequency of 100 kHz, the permittivity of the thin films deposited at various oxygen pressures is 34, 223 and 5630, respectively. Figure 5 shows the po-

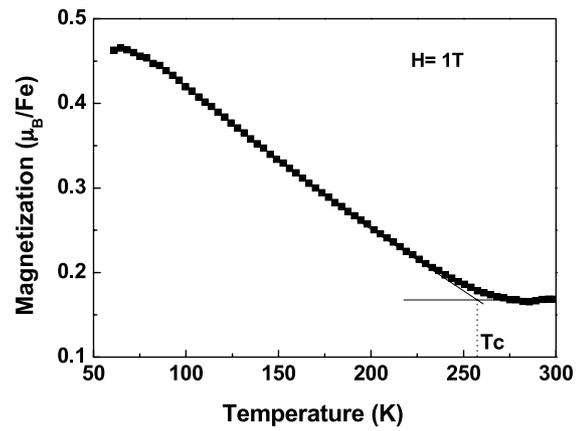


FIGURE 6 Temperature dependence of magnetization for GaFeO₃ thin film deposited at 10 Pa in zero-field cooling (ZFC) at an applied magnetic field of $H = 1$ T

larization loops of the GaFeO₃ thin films at room temperature. Obvious ferroelectric hysteresis is observed, indicating the ferroelectricity of the GaFeO₃ thin films. The asymmetrical hysteresis loops could originate from the different interface states between top and bottom interfaces [12]. Although the space group Pc_12_1n of GaFeO₃ indicates the spontaneous polarization along the b axis, the ferroelectricity has not been observed before. The observed polarization in all these GaFeO₃ thin films might be related to the strains, which resulted from the mismatch of lattice parameters and thermal expansion behavior between the film and the underlying substrate or arose from defects formed during film deposition [13, 14]. Also, from Fig. 5, the thin films deposited at lower oxygen pressures have larger polarization at the same electric field, that is $P(0.1 \text{ Pa}) > P(1 \text{ Pa}) > P(10 \text{ Pa})$.

It is well known that there are four kinds of polarization in dielectric materials: electronic polarization, atomic polarization, dipolar polarization and space-charge polarization. The above experimental results show that the electric properties of the GaFeO₃ thin films are dependent on the deposition oxygen pressures. With the decreasing of the deposition oxygen pressures, the content of oxygen vacancies in the thin films may increase and leads to the increase of leakage current. Correspondingly, the electronic polarization increases on increasing the oxygen vacancies, which induces the permittivity increase and also the polarization increase.

Furthermore, the temperature dependence of magnetization for a GaFeO₃ thin film deposited at 10 Pa in zero-field cooling (ZFC) at an applied magnetic field of $H = 1$ T is shown in Fig. 6. The magnetic transition temperature was identified at about 257 K, which is slightly higher than that for the bulk ones we reported before [8].

4 Conclusions

In summary, we have investigated the effect of deposition oxygen pressures on the crystal structure and properties of the GaFeO₃ thin films. Ferroelectricity has been observed in the GaFeO₃ thin films at room temperature. The magnetic Curie temperature is identified at about 257 K. The GaFeO₃ thin films thus could be high-temperature multiferroic materials.

ACKNOWLEDGEMENTS The authors would like to acknowledge the financial support of the National Natural Science Foundation of China (60371032).

REFERENCES

- 1 N.A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000)
- 2 T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano, Y. Tokura, *Phys. Rev. B* **67**, 180401 (2003)
- 3 N. Hur, S. Park, P.A. Sharma, J.S. Ahn, S. Guha, S.-W. Cheong, *Nature* **429**, 392 (2004)
- 4 T. Arima, D. Higashiyama, Y. Kaneko, J.P. He, T. Goto, S. Miyasaka, T. Kimura, K. Oikawa, T. Kamiyama, R. Kumai, Y. Tokura, *Phys. Rev. B* **70**, 064426 (2004)
- 5 J.H. Jung, M. Matsubara, T. Arima, J.P. He, Y. Kaneko, Y. Tokura, *Phys. Rev. Lett.* **93**, 037403 (2004)
- 6 A.M. Kalashnikova, R.V. Pisarev, L.N. Bezmaternykh, V.L. Temerov, A. Kirilyuk, T. Rasing, *JETP Lett.* **81**, 452 (2005)
- 7 D.C. Kundaliya, S.B. Ogale, S. Dhar, K.F. McDonald, E. Knoesel, T. Osedach, S.E. Lofland, S.R. Shinde, T. Venkatesan, J. Magn. Mater. **299**, 307 (2006)
- 8 Z.H. Sun, B.L. Cheng, S. Dai, L.Z. Cao, Y.L. Zhou, K.J. Jin, Z.H. Chen, G.Z. Yang, *J. Phys. D* **39**, 2481 (2006)
- 9 E.A. Wood, *Acta Cryst.* **13**, 682 (1960)
- 10 X. Qi, J. Dho, R. Tomov, M.G. Blamire, J.F. Scott, N.D. Mathur, *Appl. Phys. Lett.* **86**, 062903 (2005)
- 11 Y.P. Wang, L. Zhou, M.F. Zhang, X.Y. Chen, J.M. Liu, Z.G. Liu, *Appl. Phys. Lett.* **84**, 1731 (2004)
- 12 K.J. Choi, M. Biegalski, Y.L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y.B. Chen, X.Q. Pan, V. Gopalan, L.-Q. Chen, D.G. Schlom, C.B. Eom, *Science* **306**, 1005 (2004)
- 13 J. Lee, C.H. Choi, B.H. Park, T.W. Noh, J.K. Lee, *Appl. Phys. Lett.* **72**, 3380 (1998)
- 14 J.H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y.L. Li, S. Choudhury, W. Tian, M.E. Hawley, B. Craigo, A.K. Tagantsev, X.Q. Pan, S.K. Streiffer, L.Q. Chen, S.W. Kirchoefer, J. Levy, D.G. Schlom, *Nature* **430**, 758 (2004)