

Magnetolectric CoFe_2O_4 -lead zirconate titanate thick films prepared by a polyvinylpyrrolidone-assisted sol-gel method

Jian-guo Wan,^{a),b)} Hao Zhang, Xiuwei Wang, Dengyu Pan, Jun-ming Liu,^{a)} and Guanghou Wang

Laboratory of Solid State Microstructures, Department of Physics, Nanjing University, Nanjing 210093, China and International Center for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China

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Magnetolectric CoFe_2O_4 -PZT (lead zirconate titanate) films as thick as $1\ \mu\text{m}$ have been prepared by spin coating using a PZT sol-gel solution containing polyvinylpyrrolidone and CoFe_2O_4 powder. X-ray diffraction result reveals that there exists no chemical reaction or phase diffusion between the CoFe_2O_4 and PZT phases. The scanning electron microscopy observation confirms that the composite thick film is crack-free and has a well-defined microstructure. The composite thick films exhibit good magnetic and ferroelectric properties, as well as distinct magnetolectric coupling behavior. The magnetolectric coupling mechanism for the present composite thick film is discussed in detail. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357589]

In the past several years, there has been an increased interest in magnetolectric materials in which a spontaneous polarization could be generated as a response to an external magnetic field and vice versa.^{1–3} They facilitate conversion between energies stored in magnetic and electric fields for wide applications in sensor, actuator, transducers, etc.^{4–6} Recently, the development of magnetolectric films has become the subject of considerable attention due to their potential applications in microelectromechanical systems (MEMSs).⁷ Some deposition techniques such as pulsed laser deposition,^{8–10} composition spreads,¹¹ and sol-gel process¹² have been used to fabricate various magnetolectric films. The developed magnetolectric films include some natural multiferroic system [e.g., BiFeO_3 (Ref. 8) and BiMnO_3 (Ref. 13)] and composites by combining ferroelectric phase with ferromagnetic phase [e.g., CoFe_2O_4 - BaTiO_3 ,⁹ CoFe_2O_4 - PbTiO_3 ,¹¹ and CoFe_2O_4 -PZT (lead zirconate titanate)¹²]. The thickness of all these reported films is in the range of 30–400 nm. Although the MEMS devices are generally based on the films with thickness of $<1\ \mu\text{m}$, many potential applications require the film thickness of a micrometer or more.

In general, the limiting thickness of a crack-free magnetolectric film using conventional methods is less than $\sim 400\ \text{nm}$. Beyond this limiting thickness, a great deal of cracks will be generated due to the large mechanical stress arising from the film shrinkage during annealing. So it is difficult to prepare a crack-free magnetolectric film thicker than $1\ \mu\text{m}$ using conventional methods. To our knowledge, few investigations have been conducted on the magnetolectric thick films up to now. In this letter, we report a novel polyvinylpyrrolidone (PVP)-assisted sol-gel process for preparing the composite CoFe_2O_4 -PZT thick film on a platinumized silicon substrate. By dispersing CoFe_2O_4 powder into PZT sol-gel matrix solution, CoFe_2O_4 -PZT film as thick as $1\ \mu\text{m}$ has been successfully synthesized. The composite thick film exhibits well-defined microstructure, good ferro-

electric and magnetic properties, as well as distinct magnetolectric effect.

In this work, $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ was used for the PZT matrix. The starting PZT sol-gel matrix solution was prepared using a modified sol-gel method containing PVP (K-30) with average molecular weight of 4.0×10^4 . The appropriate portions of lead acetate trihydrate [$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$], zirconium nitrate pentahydrate [$\text{Zr}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$], tetrabutyl titanate [$\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$], and PVP were firstly dissolved in 2-methoxyethanol, respectively, and then were mixed together and stirred continuously to form a 0.4M of PZT sol-gel solution. The molar ratio of Pb:Zr:Ti:PVP was 1.1:0.52:0.48:1. The molar ratio for PVP was defined for the monomer. The CoFe_2O_4 powder was prepared by a mechanochemical method. A 0.3M of starting precursor solution with molar composition of iron nitrate [$\text{Fe}(\text{NO}_3)_3$]:cobalt nitrate [$\text{Co}(\text{NO}_3)_2$]:citric acid [$\text{C}_6\text{H}_8\text{O}_7$] = 1:2:3 was used. After the precursor was successively dried at $70\ ^\circ\text{C}$, calcined at $350\ ^\circ\text{C}$ for 30 min, and ball milled for 72 h, the CoFe_2O_4 powder with average size of $\sim 140\ \text{nm}$ was finally obtained.

The CoFe_2O_4 powder was subsequently dispersed into the PZT sol-gel matrix solution to form a suspension slurry by continuous and intensive ultrasonic mixing. The CoFe_2O_4 volume content in the slurry is $\sim 25\%$. Due to the existence of PVP, the viscosity of sol-gel solution is so large that the CoFe_2O_4 powder was quite stable in the slurry. The slurry was spin coated onto the Pt/Ti/SiO₂/Si substrate at a spinning rate of 1600 rpm for 30 s. Then the gel film was successively dried at $80\ ^\circ\text{C}$ for 6 min and at $300\ ^\circ\text{C}$ for 4 min. This spin-coating/drying procedure was repeated two times. After that, two-layer pure PZT thin gel films with each layer thickness of $\sim 50\ \text{nm}$ were deposited onto the thick film by a conventional sol-gel process. This treatment will fill the pore and prevent the appearance of the cracks in the thick film. Finally, the film was annealed at $700\ ^\circ\text{C}$ for 8 min under the oxygen atmosphere by the rapid annealing process, and the CoFe_2O_4 -PZT composite thick film with thickness of $\sim 1\ \mu\text{m}$ was obtained.

The crystalline phase of the composite thick film was analyzed by x-ray diffraction (XRD) on a D/MAX-RA diffractometer using Cu $K\alpha$ radiation. Figure 1 shows the typi-

^{a)} Authors to whom correspondence should be addressed.

^{b)} Electronic mail: wanjg@nju.edu.cn

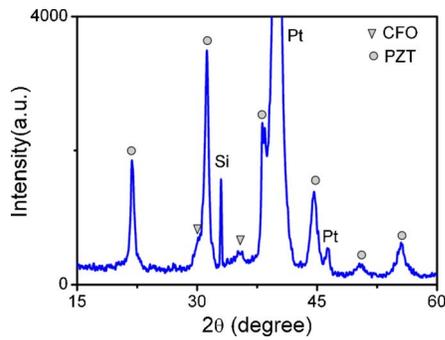


FIG. 1. (Color online) XRD pattern of the CoFe_2O_4 -PZT composite thick film.

cal XRD pattern of the film. Two distinct sets of diffraction peaks are observed, corresponding to the perovskite PZT and spinel CoFe_2O_4 phases, respectively. The XRD result reveals that there exists no chemical reaction or phase diffusion between the CoFe_2O_4 and PZT phases. In addition, both phases are polycrystalline structures. The microstructure observation for the film was carried out using a scanning electron microscopy (SEM) (LEO-1530VP). Figure 2 shows the typical SEM image of the film, revealing that it is crack-free and has a granular structure without any pore. The CoFe_2O_4 particles with average diameter of ~ 140 nm are randomly and uniformly distributed in the PZT matrix. The volume fraction of the CoFe_2O_4 particles calculated using the SEM image is ~ 0.21 , which is in agreement with that in the original sol-gel slurry. Moreover, the size of the CoFe_2O_4 particles in the film is almost the same as that of the original CoFe_2O_4 powder, indicating that the CoFe_2O_4 particles embedded in the PZT matrix did not aggregate with each other throughout overall preparation.

The formation of this dense and crack-free microstructure for the present composite thick film greatly benefits from the addition of PVP polymer and introduction of CoFe_2O_4 powder in the sol-gel solution. PVP plays an important role during the thick film preparation.¹⁴ It could be hybridized with organometallic precursors at molecular scale through strong hydrogen bonding between the C=O groups of the PVP and the OH groups of the organometallic precursors, which efficiently prevents the crack formation through the retardation of the condensation reaction and the promotion of structural relaxation in the film. Moreover, the OH groups are also present on the surface of the CoFe_2O_4 powders.¹⁵ Therefore, with the introduction of CoFe_2O_4 powders into the sol-gel solution containing PVP, the film forms strongly bonded network linked with the sol gel, the ceramic powders and the substrate, which makes it less

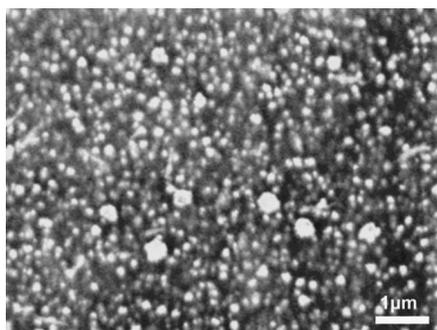


FIG. 2. Typical SEM image of the CoFe_2O_4 -PZT composite thick film.

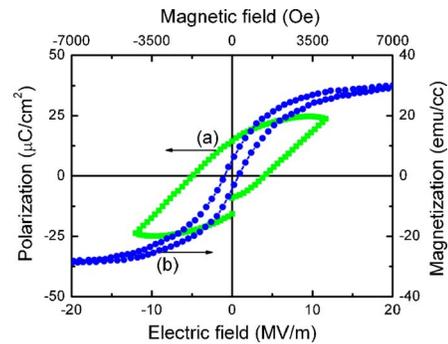


FIG. 3. (Color online) (a) Polarization-electric field hysteresis loop and (b) magnetic hysteresis loop of the CoFe_2O_4 -PZT composite thick film.

likely that the film will crack during annealing. In addition, we also note the key role of the residual PVP after pyrolysis and the CoFe_2O_4 powder in the phase formation of PZT matrix. In detail, they could act as the seeds for the nucleation of PZT crystal during annealing; thereby the preferential oriented growth of PZT controlled by usual nucleation step¹⁶ was broken, leading to the final formation of randomly oriented polycrystalline structure for the PZT matrix.

The ferroelectric hysteresis loop of the film, as shown in Fig. 3(a), was characterized using a ferroelectric test unit (RT66A, Radiant Technologies) at 60 Hz. The remanent polarization (P_r) and coercive field (E_c) were found to be, respectively, $\sim 14.6 \mu\text{C}/\text{cm}^2$ and ~ 4.3 MV/m at an applied maximum electric field of 12 MV/m, which were comparable to the PZT- CoFe_2O_4 thin film with similar molar components. The field dependent magnetization at room temperature for the film was evaluated on a superconducting quantum interference device magnetometer. Figure 3(b) presents the magnetic hysteresis loop for the film under the applied magnetic field parallel to the film plane. The film exhibits a well-defined magnetic hysteresis loop. The saturation magnetization (M_s) and coercive field (H_c) are, respectively, ~ 28.4 emu/ cm^3 and ~ 0.33 kOe. Such low M_s value for the composite film is reasonable since it significantly depends on the concentration of CoFe_2O_4 particles in composite film, which is only ~ 0.21 in this work. The H_c value for the present composite thick film is surprisingly much lower than that of the pure CoFe_2O_4 film,¹⁷ which is possibly attributed to the large residual stress in CoFe_2O_4 due to the lattice mismatch and thermal expansion coefficient difference between the PZT and CoFe_2O_4 phases. This easy-magnetization characteristic is beneficial to the enhancement of magnetoelectric coupling between the ferroelectric and ferromagnetic phases at low magnetic field.

The magnetoelectric voltage coefficient $\alpha_E = dE/dH$, which is characterized by the induced electric field E under an applied magnetic field H , was then measured as function of dc magnetic bias H_{bias} for the composite thick film. $H = 10$ Oe was generated by a pair of Helmholtz coils and H_{bias} up to 6 kOe was generated by an electromagnet. Both of them were superimposed and parallel to the film plane. The induced electric field E was measured using a lock-in amplifier (SRS Inc., SR830). Figure 4 plots the variation of α_E with H_{bias} at a fixed ac magnetic frequency of $f = 10$ kHz. It is clear that the composite thick film exhibits distinct magnetoelectric effect which significantly depends on H_{bias} . As shown in Fig. 4, the film has a small initial α_E value of ~ 5 mV/cm Oe near zero magnetic bias. At low

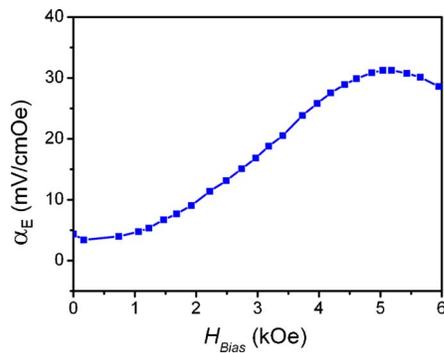


FIG. 4. (Color online) Variation of α_E with H_{bias} at magnetic frequency $f=10$ kHz for the CoFe_2O_4 -PZT composite thick film.

$H_{\text{bias}} < 1$ kOe, the α_E value increases very slowly with increasing H_{bias} . As H_{bias} is over ~ 1 kOe, the α_E value starts to quickly increase with increasing H_{bias} , until it achieves 30 mV/cm Oe at $H_{\text{bias}}=4.5$ kOe. Then the α_E value tends to saturation after H_{bias} is above ~ 4.5 kOe.

The magnetoelectric coupling behavior for the present composite thick film is different from that for the reported composite thin films and composite bulks,^{12,18} though their magnetoelectric coupling mechanisms are all the same, essentially being attributed to the magnetic-mechanical-electric coupling interaction between the magnetostrictive and ferroelectric phases through the stress-mediated transfer in the interface. This coupling interaction starts with the domain-wall motion and domain rotation of the magnetostrictive phase (e.g., CoFe_2O_4), which is sensitive to the residual stress, spontaneous polarization, and magnetization in the system, consequently determining the magnetoelectric coupling behavior of the composite. For the composite bulk, it is well known that there exists little residual stress, spontaneous polarization, or magnetization; thereby its magnetoelectric coupling behavior generally complies with the usual H_{bias} dependence of the piezomagnetic coupling coefficient $q = \delta\lambda / \delta H_{\text{bias}}$ (where λ is the magnetostriction).^{2,18} In other words, it possesses an optimized $H_{\text{bias}} < 1$ kOe at which the α_E value is maximum, and the α_E value quickly decreases if H_{bias} is far away from the optimized H_{bias} . As for the composite film, the case is distinctly different. Due to the unique film-on-substrate structure, the film is seriously clamped by the substrate.³ Moreover, there exist the lattice mismatch and thermal expansion coefficient difference among the PZT, CoFe_2O_4 , and substrate. All of these factors bring about a large residual stress and result in various variations of magnetization, polarization, and piezomagnetism in the overall film, causing its magnetoelectric coupling behavior to depart from the bulk behavior. In the thin films, this effect is so serious that their magnetoelectric behavior is completely different from that of the bulk.^{10,12} On the other hand, for the present thick film, since its thickness is much larger than that of the thin film, the clamping effect of the substrate becomes weak. Consequently, the magnetoelectric coupling behavior starts to transform toward the bulk behavior, exhibiting an analogous α_E dependence on H_{bias} . Meanwhile, as the depressing effect of the substrate still partially exists, it is difficult for the α_E value for the thick film to achieve saturation at lower H_{bias} and its optimized H_{bias} was retarded to a higher value of ~ 4.5 kOe. On the other hand, the easy-

magnetization characteristic with quite lower H_c value for the thick film brings about a small initial α_E value near zero magnetic bias, which is similar to that of the thin film,¹² indicating that the thick film still possesses the magnetoelectric coupling behavior of the thin film at certain degree. In addition, the ferromagnetic particle concentration in the ferroelectric matrix also significantly affects the magnetoelectric effect of the composite film.¹⁸ Further work will be done to investigate the effect of the film thickness and ferromagnetic particle concentration on the magnetoelectric coupling behavior for the thick film.

In summary, magnetoelectric CoFe_2O_4 -PZT composite thick films have been deposited on Pt/Ti/SiO₂/Si substrate by spin coating using a PZT sol-gel solution containing PVP and CoFe_2O_4 powder. The film is as thick as 1 μm , being crack-free with well-defined microstructure. The present composite thick films exhibit good magnetic and ferroelectric properties, as well as distinct magnetoelectric coupling behavior. This work will facilitate the applications of magnetoelectric material on MEMS devices.

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¹T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, *Nature* (London) **426**, 55 (2003).

²G. Srinivasan, E. T. Rasmussen, J. Gallegos, R. Srinivasan, Yu. I. Bokhan, and V. M. Laletin, *Phys. Rev. B* **64**, 214408 (2001).

³C. W. Nan, G. Liu, Y. H. Lin, and H. Chen, *Phys. Rev. Lett.* **94**, 197203 (2005).

⁴S. X. Dong, J. R. Cheng, J. F. Li, and D. Viehland, *Appl. Phys. Lett.* **83**, 4812 (2003).

⁵J. G. Wan, J.-M. Liu, G. H. Wang, and C. W. Nan, *Appl. Phys. Lett.* **88**, 182502 (2006).

⁶J. Ryu, A. V. Carazo, K. Uchino, and H. E. Kim, *Jpn. J. Appl. Phys., Part 1* **40**, 4948 (2001).

⁷W. Prellier, M. P. Singh, and P. Murugavel, *J. Phys.: Condens. Matter* **17**, R803 (2005).

⁸J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).

⁹H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Roytburd, and R. Ramesh, *Science* **303**, 661 (2004).

¹⁰J. P. Zhou, H. C. He, Z. Shi, and C. W. Nan, *Appl. Phys. Lett.* **88**, 013111 (2006).

¹¹K. S. Chang, M. A. Aronova, C. L. Lin, M. Murakami, M. H. Yu, J. Hatrick-Simpers, O. O. Famodu, S. Y. Lee, R. Ramesh, M. Wuttig, I. Takeuchi, C. Gao, and L. A. Bendersky, *Appl. Phys. Lett.* **84**, 3091 (2004).

¹²J. G. Wan, X. W. Wang, Y. J. Wu, M. Zeng, Y. Wang, H. Jiang, W. Q. Zhou, G. H. Wang, and J. M. Liu, *Appl. Phys. Lett.* **86**, 122501 (2005).

¹³W. Eerenstein, F. D. Morrison, J. F. Scott, and N. D. Mathur, *Appl. Phys. Lett.* **87**, 101906 (2005).

¹⁴H. Kozuka and M. Kajimura, *J. Am. Ceram. Soc.* **83**, 1056 (2000).

¹⁵D. A. Barrow, T. E. Petroff, R. P. Tandon, and M. Sayer, *J. Appl. Phys.* **81**, 876 (1997).

¹⁶K. C. Chen and J. D. Mackenzie, *Mater. Res. Soc. Symp. Proc.* **180**, 663 (1990).

¹⁷S. D. Sathaye, K. R. Patil, S. D. Kulkarni, P. P. Bakre, S. D. Pradhan, B. D. Sarwade, and S. N. Shintre, *J. Mater. Sci.* **38**, 29 (2003).

¹⁸M. Zeng, J. G. Wan, Y. Wang, H. Yu, J.-M. Liu, X. P. Jiang, and C. W. Nan, *J. Appl. Phys.* **95**, 8069 (2004).