Correlating phonon frequency shift with magnetoelectric effect in the PbTiO₃-CoFe₂O₄ multiferroic system due to interfacial stress

Chih-Ya Tsai¹, Tung-Ching Huang², and Wen-Feng Hsieh^{1,3}

¹National Chiao Tung University, Department of Photonics and Institute of Electro-Optical Engineering 1001 Tahsueh Rd., Hsinchu 300, Taiwan Phone: 886-3-5712121-56310 E-mail: wfhsieh1955@gmail.com ²National Taiwan Normal University, Department of Physics

88, Sec.4, Ting-Chou Rd., Taipei 116, Taiwan

³National Cheng Kung University, Institute of Electro-Optical Science and Engineering

1 Ta-Hsueh Rd., Tainan 701, Taiwan

1. Introduction

Multiferroic materials possess ferromagnetism and ferroelectricity simultaneously and allow coupling between the two order-parameters [1]. The magnetoelectric coupling (ME effect), which means a change of polarization in response to magnetic fields or vice versa, is transmitted by elastic interaction and interfacial stress along two phases boundaries [2]. With a scale of single atomic boundary, the polarization and magnetization will reconstruct by chemical hybridization, strain effect and ME interaction. Phonon at boundary is, moreover, sensitive to residual stress, structure variation, and polarization states [3]. However, little is known about the phonon behaviors in multiferroic even though in the past it played a crucial role in understanding of classical ferroelectrics. In our work, we propose a micro-Raman detection method to measure the coupled interactions across micro hetero-interfaces. Not only the stress dependence of phonon shifting at the interface is observed but also the distinct magnetic properties in M-H hysteresis are discussed in three different geometrical CoFe₂O₄-PbTiO₃ multiferroic systems.

2. Methods of fabrication

We fabricated three geometrical types of multiferroic on Pt/Si by sol-gel and spin-coating methods. They were respectively the 0-3 type with CoFe₂O₄ (CFO) particles embedded in PbTiO₃ (PTO) matrix, the 2-2 type with CFO and PTO nanolayers, and the disk-3 type with CFO disc aligned in PTO matrix as illustrated in fig. 1. The PTO gel and CFO gel was made by the following methods [2]. PTO films on Pt/Si, PTO powder, and CFO powder were also fabricated as the reference samples. The disk-3 sample was prepared by alternatively spin-coating and drying PTO and CFO layers [2]. A process of making the 2-2 type was the same as the disk-3 type except that every layer was individually annealed at 500 $^{\circ}$ C for 3 minutes. The 0-3 type was made by mixing CFO particles with PTO solution and then spin-coating on Pt/Si. Finally, all the samples were annealed at 750 °C for 1.5 hrs. The properties of multiferroics were confirmed by X-ray diffraction (XRD), using a Mac science M18X X-ray diffractometer equipped with a rotating anode (Cu-k α line of 1.5405 Å) at room temperature (RT). The magnetic properties were measured by superconducting quantum interference device (SQUID, MPMS-XL)system. The micro-Raman measurement was performed by using an Ar-ion laser with 488 nm at RT.



Fig. 1 (Left) Schematic illustration of three multiferroics with different connectivity schemes: (a) the 0-3 type with CFO particles embedded in PTO matrix, (b) the 2-2 type with CFO and PTO nanolayers, (c) the disk-3 type with CFO disc aligned in PTO matrix, and (d) top-view image of SEM of the disk-3 film. Fig. 2 (Right) Micro-Raman spectra of disk-3 (blue), 2-2 (orange), 0-3 (red) multiferroics, PTO/Pt/Si (green), and PTO powder (black) for comparison.

Table I. Refined lattice parameters for the PTO powder, PTO/Pt/Si, CFO powder, and three multiferroics, where the strain is defined as variation in lattice constant from the bulk crystals.

Samples	РТО		CFO	
	I(100) / I(001)	c/a	a(Å)	Strain (%)
PTO powder	1.988	1.041		
PTO/Pt/Si	2.372	1.024		
CFO powder			8.387	
Disk-3	2.903	1.027	8.362	-0.302
0-3	3.162	1.012	8.386	-0.008
2-2	3.693	1.009	8.366	-0.253

3. Results and discussions

XRD and Interfacial stress

The XRD patterns of all the samples reveal the correct phases of PTO and CFO without secondary phases (not shown here). The lattice parameters of the samples are listed in Table I after refining the XRD data. The intensity ratio of $I_{(100)}/I_{(001)}$ for pure PTO powders is close to 2, indicating the random orientation. However, the ratio is larger for the 2-2 type than that for the disk-3type. It indicates the *c*-axis of PTO in the 2-2 type prefers to orient in in-plane

direction while it prefers growing vertically in the disk-3 film [3]. Lowering trend of c/a also indicates that the ferroelectricity in multiferroics decreased. The strain of CFO is -0.305, -0.253, and -0.08% for the disk-3, 2-2, and 0-3 types, respectively. Hence, the stress along multiferroic boundary is most serious in the disk-3 type and least in the 0-3 type. The strain states of PTO are not discussed since PTO connects with both Pt/Si substrates and CFO. It is hard to verify the originations of stress from substrates or CFO.

Raman spectra and Lattice dynamics

Fig. 2 shows the Raman spectra of PTO powders, PTO/Pt/Si, and three multiferroics on Pt/Si at RT. PTO belongs to the $C_{4v}^1(P4mm)$ space group with tetragonal phase at RT [3] and is easily detected. However, CFO with $O'_{\rm h}(Fd3m)$ space group and inverse spinel structure [4] is hardly detected. Hence, we concentrate on spectra of PTO. According to the assignments of Foster et al. [3], PTO has 3A1(TO), 3E(TO), 3A1(LO), and 3E(LO) Raman active modes. For all multiferroic films, $A_1(1TO)$, $A_1(2TO)$, and $A_1(3TO)$ modes with frequencies at 150, 350, and 630 cm⁻¹ shift and broad significantly towards lower energy regions by comparing with PTO powders. The spectrum of PTO/Pt/Si lacks change illustrates the red-shifting can't be due to the interactions between PTO and Pt/Si. Besides, XRD results confirm there is no substituting effect. Hence, we ascribe the red-sifting of $A_{i}(TO)$ modes to the interfacial stress between PTO and CFO. The E modes, representing atomic vibrations in a and b axes, only move little. However, atomic motions along *c*-axes specified as $A_{1}(TO)$ modes change a lot. For this reason, the atomic bonding and ME interactions between CFO and PTO should be particular planes along c-axes [5]. Furthermore, the Raman frequencies of the disk-3 type shift most than that of the others. It indicates the disk-3 film has intense coupling between two ferrite materials agreeing with XRD and magnetic results.

Magnetic properties and ME interactions

Fig. 3 shows the in-plane magnetization measurements at RT for different geometrical CFO contained multiferroics. The coercivity (H_C) and magnetized loops of CFO are similar to that of 0-3 film due to the same fabricating processes. In our study, the magnetic properties of multiferroics differing from ferromagnetic materials owing to the interfacial interaction with ferroelectric materials are summaries as following: First, the in-plane saturation magnetization (Ms) of disk-3 and 2-2 types are hard to saturate compared with that of 0-3 types as shown in the inset of Fig. 3. It is due to the feedback of ME interaction under high magnetic fields. Since the magnetic field will induce a polarization by ME effect, the polarization will also turn to affect the magnetization when the magnetic field is large. Finally, Ms is hard to reach saturated states as a result of ME interactions. Second, H_C becomes small in the disk-3 film. For example, H_{C} are about 1.01, 1.51, and 0.20 kOe for the 0-3, 2-2, and disk-3 types, respectively. It is ascribed to fuzzy defects proposed by O'Handley [6]. In fuzzy defect model, H_C decreases with increasing defect size where fuzzy defect is defined by strain fields. Third, H_C at left hand side is not consistent with that at right hand side. The percentages of variation of in-plane H_C are 34.14, 26.37, and 4.44% for the disk-3, 2-2, and 0-3 types. H_C of the disk-3 and 2-2 types are more nonsymmetrical than that of the 0-3 type. The nonsymmetrical phenomenon is due to an initial magnetization on CFO induced by the electric field of PTO through ME effect. Finally, in contrast to the 0-3 and 2-2 types, the disk-3 type is hard to reach Ms and its H_C is lower and nonsymmetrical due to the strong compressive stress and ME effect at the PTO/CFO interfaces.



Fig. 3 The local magnification of in-plane hysteresis loops for the 0-3 (red), 2-2 (blue), and disk-3 (black) samples where the inset is the complete M-H loops under a magnetic field up to 20 kOe.

4. Conclusions

The characteristics of three different geometric forms of the PbTiO₃-CoFe₂O₄ multiferroics fabricated by simple sol-gel methods are investigated using FESEM, XRD, Raman spectroscopy, and SQUID. For different geometric multiferroics, the magnetic properties and interfacial phonon behaviors depend on different degrees of interfacial stress, chemical bonding, and ME interactions along CFO/PTO interfaces. Disk-3 types, the self-assembled CFO disks embedded in PTO matrix, have larger nonsymmetrical coercivity (H_C) and unsaturated magnetization (Ms) also show the largest shift in $A_1(2TO)$ and $A_1(3TO)$ modes than the other types such as CFO and PTO multilayered structures (2-2 types) and CFO particles embedded in PTO matrix (0-3 types).

Acknowledgements

This work is partially supported by the National Science Council of Taiwan under grant NSC-96-2628-M-009-001-MY3 and NSC-95-2221-E-133-001.

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