Electric control of magnon frequencies and magnetic moment of bismuth ferrite thin films at room temperature

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(Received 16 May 2011; accepted 21 July 2011; published online 10 August 2011)

Here, we report the tuning of room-temperature magnon frequencies from 473 GHz to 402 GHz (14%) and magnetic moment from 4 to 18 emu/cm³ at 100 Oe under the application of external electric fields (E) across interdigital electrodes in BiFeO₃ (BFO) thin films. A decrease in magnon frequencies and increase in phonon frequencies were observed with Magnon and phonon Raman intensities are asymmetric with polarity, decreasing with positive E (+E) and increasing with negative E (−E) where polarity is with respect to in-plane polarization P. The magnetoelectric coupling (α) is proved to be linear and a rather isotropic $\alpha = 8.5 \times 10^{-12}$ sm^{−1}. © 2011 American Institute of Physics. [doi:10.1063/1.3624845]

Two device aims for magnetoelectric (ME) multiferroics are switching of polarization by magnetic fields and of magnetization by electric field. The first effect is useful for magnetic field sensors and for memory elements if, for example, polarization switching is via a very small magnetic field from a coil underneath an integrated circuit. The latter effect is suitable for nondestructive low-power, high-density magnetically read, and electrically written memory elements.^{1–9} If the system possesses additional features, such as propagating magnon (spin wave) excitations at room temperature, additional functional applications may be possible. Magnons are of course quantized spin waves, just as phonons are quantized vibrational waves, and Raman spectroscopists usually refer to magnon frequencies, magnon-phonon coupling, etc., whereas THz engineers are more likely to use the terms spin waves and spin-phonon coupling. Magnons were first established from the T^{3/2} Bloch law¹⁰ in 1930 as quantized eigenmodes of magnetically ordered regions, later developed by Holstein and Primakoff¹¹ and Dyson.¹² Magnon-based logic systems have been initiated by various scientists, and prototype devices show potential for future complementary metal oxide semiconductor (CMOS) technology.^{13–15} The major drawback of magnon logic devices is the slow group velocity (two orders of magnitude less than speed of light) and high attenuation (six orders of magnitude higher than for photons in optical fibers), but magnetic domain velocities can be supersonic, unlike ferroelectric or ferroelastic domain walls, which gives magnetic random access memory an advantage over Ferroelectric random access memory. For practical applications, it is important that material properties should be observable in (CMOS-compatible) thin-film form and at ambient temperatures. In the present paper, we report such studies.

BiFeO₃ (BFO) is well-known room-temperature multiferroic, and recently most ME research has been centered on

it, due to very high ferroelectric polarization (100 $\mu\text{C}/\text{cm}^2$) and antiferromagnetic ordering below $T_N \sim 643$ K.^{1,2} The spins form a cycloid structure with a wavelength of $\lambda_0 = 62$ nm and cycloid wave vector $q = 2\pi/\lambda_0$. An external electric field can switch the spin waves because the cycloid lies in the ($\bar{1}2\bar{1}$) plane formed by the ferroelectric polarization P along the [111] directions.³

Magnons are well known in insulating and semiconducting materials, such as orthoferrites. ErFeO₃, Eu_{0.75}Y_{0.25}MnO₃, YMn₂O₅, and TbMn₂O₅ have shown magnon softening (frequency decrease) near spin reorientation temperatures, colossal magnon-phonon coupling, and symmetric exchange coupling mechanisms, respectively.^{16,17} Several theoretical models and predictions were carried out supporting the existence of electromagnons (spin waves coupled to polar phonons) in multiferroics.¹⁸ In 2008, Cazayous *et al.*¹⁹ and Singh *et al.*²⁰ found electromagnons in BFO single crystals, whereas Kumar *et al.*²¹ observed magnons and magnon-phonon coupling in BFO thin films. There are two magnon branches in BFO, usually denoted ϕ and λ . Rovillain *et al.* demonstrated tuning of ϕ magnon frequency about 30% and λ magnon frequency about 15% with external electric field on BFO single crystals.²² Why was such a long time taken to show the electric control of BFO magnons? One answer lies in the difficulty to observe magnons at room temperature; this can be used to monitor switching.

Here, we report the electric control of room temperature magnons and magnetic moments of BFO thin films grown by pulsed laser deposition techniques on pre-patterned interdigital electrodes (IDs) with average height (150 $\pm$ 25 nm). Surface effects are prominent in our investigation. We also show the magnon-phonon coupling and its behavior under electric field.

Pre-patterned platinum IDs was procured from NASA Glenn Research Center's electronics division having dimension 1900 μm (length), 15 μm (interdigital spacing), and 150 $\pm$ 25 nm (height) with 45 parallel capacitors in series on sapphire substrates. Fig. 1 shows the scanning electron

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FIG. 1. (Color online) Scanning electron microscope image of pre-patterned interdigital electrode deposited with BFO by PLD techniques. The dimension of the electrodes was $1900\ \mu\text{m}$ (length), $15\ \mu\text{m}$ (inter digital spacing), and $150 \pm 25\ \text{nm}$ (height).

microscopy (SEM) image. An excimer laser (KrF, $248\ \text{nm}$) with a laser energy density of $1.5\ \text{J}/\text{cm}^2$ and pulse repetition rate of $10\ \text{Hz}$ was used to deposit the BFO films. During deposition, the substrate was maintained at 650°C and oxygen pressure at $80\ \text{mTorr}$. The orientation and phase purity of the films were characterized by x-ray diffraction (XRD) using Cu K_α radiation in a Siemens D500 diffractometer. Micro-Raman spectra were recorded in the backscattering geometry using $514.5\ \text{nm}$ monochromatic radiations. The magnetization hysteresis loop $M(H)$ measurements were carried out using a vibrating sample magnetometer (VSM) (Lakeshore 7407).

Fig. 1 shows the SEM image of as-grown BFO films on interdigital electrodes. The dimension of samples fitted well onto the VSM probe for magnetization measurements. XRD and Raman spectra imply the formation of single-phase polycrystalline BFO thin films, but XRD data of the bare electrode itself possess a lot of peaks due to electrode processing. SEM images of BFO/ID displayed homogeneous surface topography of the film. Raman spectra is a powerful tool to detect impurities even at the local level, and different regions of the BFO/ID showed similar Raman spectra that matched well with those of single-crystal and polycrystalline BFO thin films. Laser light was focused between the two electrodes, and the surface of the film was parallel with the electrode height (no steps) so that applied electric field uniformly lay across the electrodes.

Details of BFO Raman modes were discussed in the past by our group.^{20,21,23} We observed five strong Raman-active modes in the low-frequency region: 72 , 139 , 170 , 212 , and $266\ \text{cm}^{-1}$, along with the soft electromagnon at $15.8\ \text{cm}^{-1}$ (Fig. 1(a)). Eight weak Raman-active modes were also observed around 361 , 476 , 523 , 605 , 680 , 824 , 940 , and $1091\ \text{cm}^{-1}$ (not shown here). Since we observed only one electromagnon branch, our discussion will be limited to this mode. Fig. 2 shows the electric field dependent low-frequency magnons and phonons. It can be clearly seen that the magnon intensity decreases with increase in electric field; this effect was more prominent above the coercive field E_c of

FIG. 2. (Color online) Electric tuning of frequencies of magnons and lowest-energy phonons. The direction of arrows indicates the direction of applied field with respect to ferroelectric in-plane polarization: $-E$ represents the $-Ve$ applied field; downward arrows indicate decreases in intensity, whereas upward arrows show increases in intensity.

BFO, and similar effects were observed for the lowest phonon modes for $+E$ (sign with respect to in-plane polarization P), whereas the reverse phenomenon was visible for negative bias $-E$. The magnon and phonon intensities are related to the dielectric susceptibility²⁴ through the fluctuation-dissipation theorem. Experimental results were analyzed by using calculations of integrated reduced Raman scattering given by: $S = \int_{\omega_1}^{\omega_2} I/[n(\omega) + 1]^{d\omega}$, where ω_1 and ω_2 are the limits of Raman bands and $n(\omega)$ is the Bose population factor. The change in magnon Raman intensity under external field is via the influence of E on phonons, implying strong magnetoelectric coupling. The lowest phonon branches at 76.1 and $71.1\ \text{cm}^{-1}$ are a split pair of A_1 and E -symmetry transverse modes that would be degenerate if BFO were cubic. Under application of an external field, the lowest A_1 mode at $71.1\ \text{cm}^{-1}$ shifted up toward the E mode; however, a weak shoulder persists even at maximum applied electric field. This is because A_1 modes must have polarization along the ferroelectric polarization and an external electric field rotates

FIG. 3. (Color online) Change in magnon and phonon frequencies under applied external electric field: (a) change in magnon frequencies with $-Ve$ electric field; (b) change in magnon frequencies with $+Ve$ electric field; (c) change in lowest phonon frequency with $-Ve$ electric field; and (d) change in lowest phonon frequency with $+Ve$ electric field.

FIG. 4. (Color online) $M(H)$ hysteresis at 295 K and 0, +180, and -180 kV/cm applied electric field; inset shows the linear change in magnetization under external electric field.

that towards the xy -plane, making the A_1 mode more like the E-symmetry modes: the Coulomb force overcomes the crystalline anisotropy.

The origin of magnons and the phonon-magnon model have been discussed in our earlier reports.^{21,23} For a quantitative analysis, the magnon and phonon modes were fitted with a damped harmonic oscillator model (DHO) at constant temperature for various electric fields;²⁵ fitted data are shown in the Fig. 3. One thing was common in all the fitted data: we observed no significant change in magnon and phonon frequency below the coercive field of BFO, suggesting the importance of domain walls. Moreover, the magnon frequency did not recover completely after removal of external maximum electric field (a memory effect, probably also related to domain walls and their pinning). The behavior of magnon frequency under positive and negative bias was not symmetric. The magnon frequencies decrease a maximum of 3 cm^{-1} ($\sim 90 \text{ GHz}$, i.e. 15%) under the application of external field. The lowest doubly degenerate E-mode was practically unaffected by the electric field, whereas the transverse optic A_1 increased frequency, and it seem to merge with the E-mode. We infer from this a switching of domains. This electric tuning of magnon frequencies by about 15% may be helpful for design of real magnon logic device elements and especially devices in the 0.4-0.5 THz range.

Fig. 4 shows the electric control of magnetic moments. It can be readily seen that, in zero field, the $M(H)$ curve passes almost through the exact origin, implying a non-ferromagnetic behavior of BFO thin films. There is a small irregularity in some $M(H)$ curves, due to very high diamagnetic signal from the sapphire substrate. However, under external electric field greater than the coercive field E_c , $M(H)$ behaves well and shows large hysteretic opening in the $M(H)$ loop with a low coercive field and high remanent magnetization. An insignificant opening in $M(H)$ loops was observed below the coercive electric field. Significantly, we observe that the remanent magnetization changes linearly with change in

electric field and that it is asymmetric with respect to $+E$ and $-E$. Hence, a linear ME coefficient was calculated from change in magnetization (below H at 100 Oe) along parallel and perpendicular directions: calculated ME-coefficients $\alpha = \mu_0 \Delta M / \Delta E$ are nearly isotropic at $0.9 \times 10^{-11} \text{ sm}^{-1}$ and $0.8 \times 10^{-11} \text{ sm}^{-1}$, respectively. However, the $M(H)$ loop was not symmetrically switched for the $-Ve$ bias field, as mentioned above, and these values are for $+E$. Our films exhibit very low leakage current that makes it possible to apply large electric fields.

In summary, after several years of effort, a highly resistive BFO thin film was fabricated on pre-patterned platinum electrodes on sapphire substrates by periodic lattice distortion (PLD) techniques. Room-temperature magnon (spin waves) displayed tunability of 3 cm^{-1} under electric bias fields. Magnons of 380 GHz electrically shifted reversibly by about 15%. This opens a path for magnon logic elements for practical applications (room temperature, CMOS-compatible) at 0.4-0.5 THz.

This work was supported in parts by DOE-DE-FG02-08ER46526 and IFN-NSF-RII 07-01-25 Grants.

¹J. 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).

²W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature* **442**, 759 (2006).

³D. Lebeugle, D. Lebeugle, D. Colson, A. Forget, M. Viret, A. M. Bataille, and A. Gukasov, *Phys. Rev. Lett.* **100**, 227602 (2008).

⁴T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, *Nature* **426**, 55 (2003).

⁵M. Fiebig, *J. Phys. D: Appl. Phys.* **38**, R123 (2005).

⁶D. I. Khomskii, *Physics* **2**, 20 (2009).

⁷N. A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).

⁸H. Schmid, *Ferroelectrics* **162**, 317 (1994).

⁹G. Catalan and J. F. Scott, *Adv. Mater.* **21**, 2463 (2009).

¹⁰F. Bloch, *Z. Phys.* **61**, 206 (1930).

¹¹T. Holstein and H. Primakoff, *Phys. Rev.* **58**, 1098 (1940).

¹²J. F. Dyson, *Phys. Rev.* **102**, 1217 (1956).

¹³M. P. Kostylev, A. A. Serga, T. Schneider, B. Leven, and B. Hillebrands, *Appl. Phys. Lett.* **87**, 153501 (2005).

¹⁴V. V. Kruglyak, S. O. Demokritov, and D. Grundler, *J. Phys. D*, **43**, 264001 (2010).

¹⁵A. Khitun, M. Bao, and K. L. Wang, *J. Phys. D* **43**, 264005 (2010).

¹⁶N. Koshizuka and S. Ushioda, *Phys. Rev. B* **22**, 5394 (1980).

¹⁷A. B. Sushkov, R. V. Aguilar, S. Park, S. W. Cheong, and H. D. Drew, *Phys. Rev. Lett.* **98**, 027202 (2007).

¹⁸P. A. Fleury and R. Loudon, *Phys. Rev.* **166**, 514 (1968).

¹⁹M. Cazayous, Y. Gallais, A. Sacuto, R. de. Sousa, D. Lebeugle, and D. Colson, *Phys. Rev. Lett.* **101**, 037601 (2008).

²⁰M. K. Singh, R. S. Katiyar, and J. F. Scott, *J. Phys. Condens. Matter* **20**, 252203 (2008).

²¹A. Kumar, N. M. Murari, and R. S. Katiyar, *Appl. Phys. Lett.* **92**, 152907 (2008).

²²P. Rovillain, R. de Sousa, Y. Gallais, A. Sacuto, M. A. Méasson, D. Colson, A. Forget, M. Bibes, A. Barthélémy, and M. Cazayous, *Nature Mater.* **9**, 975 (2010).

²³A. Kumar, N. M. Murari, and R. S. Katiyar, *J. Raman Spectroscopy* **39**, 1262 (2008).

²⁴S. Lushnikov, S. Gvasaliya, and R. S. Katiyar, *Phys. Rev. B* **70**, 172101 (2004).

²⁵R. S. Katiyar, J. F. Ryan, and J. F. Scott, *Phys. Rev. B* **4**, 2635 (1971).