Ultrafast Magneto-Optical Spectroscopy of BiFeO3-BaTiO3 Based Structures

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ABSTRACT

Ultrafast spectroscopy can provide unique tools to study and control electronic and structural dynamics on a femtosecond time scale. Here we study, the yet little explored multiferroic material, $BaTiO_3$-$BiFeO_3$ (BTO-BFO), that has demonstrated enhanced magnetic properties, a higher DC resistance in comparison to BFO, and improved magnetoelectric coupling. Our studies include ultrafast time resolved differential reflection and optically induced birefringence.

Keywords: Multiferroics, Time Resolved Spectroscopy, Magneto-Electric Effects, BTO-BFO

1. INTRODUCTION

Phenomena where a magnetic (electric) polarization is induced via an external electric (magnetic) field, has been known for over 100 years and became the subject of more systematic studies 50 years ago. However, only recently there has been considerable renewed research interest in this phenomenon owing to the possibility of creating novel and high performance magneto-electric materials. In order to harness the full potential of the Electro-Optic (EO) and Magneto-Electric (ME) materials, the combination of sample growth, extensive characterizations, as well as theoretical modeling approaches are required.

In this work, we study a poly-crystalline $BaTiO_3$-$BiFeO_3$ (BTO-BFO), a new multiferroic material with improved magneto-electric properties. The sample has ferroelectric Curie temperature of ~1103 K and the anti-ferromagnetic Néel temperature of ~ 643 K. Our (1-x)BTO-(x)BFO (x = 0.725) is a solid state mixture. As shown in Fig. 1, X-ray measurement reveals that the film is in pure perovskite phase and exists in a single phase rather than in separate components; therefore, our observed response is a combined effect of the whole solution. The BTO-BFO films were deposited at 900 ºC on platinized (100) silicon substrate using KrF excimer pulsed laser (λ= 248 nm) deposition (PLD). A background pressure of 100 mTorr of oxygen was maintained during the growth. After the deposition, films were cooled down to room temperature with 5ºC/min ramp rate in 3 Torr oxygen pressure [1]. The mixture we have selected, address the need to reduce the electrical leakage currents due to increased conductivity from oxygen vacancies and Fe ions in BFO structures [1,2].

Our studies presented here, include ultrafast Time Resolved Differential Reflection (TRDR) and Time Resolved Optically Induced Birefringence (TROIB) at different laser fluences, where we observe tunability in both dynamics. Our optical studies provide new insights on the time scales of the interactions in this, not yet extensively explored, material system. Time resolved spectroscopy will allow us to understand the relaxation of photoexcited carriers; where after the initial photoexcitation, the nonequilibrium population of electrons and holes relax by a series of scattering processes including, carrier-carrier and carrier-phonon scattering.

For our optical measurements we used both an amplified Ti:Sapphire oscillator with a repetition rate of 1 kHz (high fluence regime), a wavelength of 800 nm, and a pulse duration of 100 fs as well as a Ti:Sapphire oscillator with a repetition rate of 80 MHz (low fluence regime). The laser pulses were split into a pump and a probe beam. The pump pulses were delayed using a moving mirror then frequency doubled to 400 nm via a BBO crystal. The probe beam has a spot size of 150-200 μm with the pump being slightly larger. The TRDR was measured to extract the pump-induced change in carrier dynamics. For our TROIB measurements, the polarization of the pump and probe pulses were set via

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half wave plates and the reflected light travels through a Wollaston prism to separate the S and P polarizations of the reflected pulses. Balanced photodiode detection was used to measure the differences between the S and P polarizations as a function of the time.

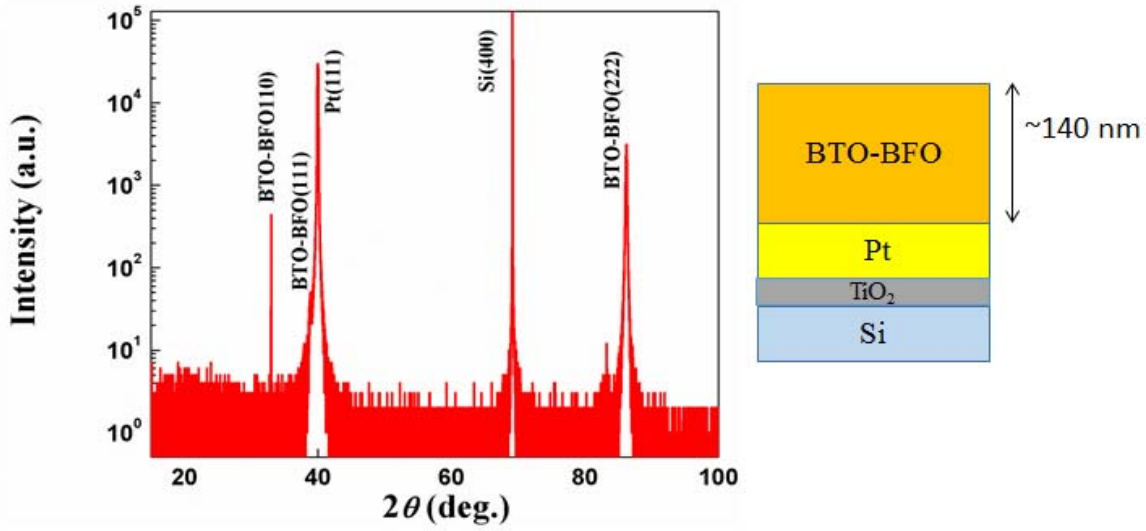

Fig. 1: X-ray diffraction of the BTO-BFO- film shows that the film is in pure perovskite phase. No pyrochlore phase is observed and the film is preferentially (111)-oriented.

The left panel in Fig. 2 shows the sample's cross-sectional Transmission Electron Microscopy (TEM) by standard focused ion beam etching technique. As shown here, the BTO-BFO consists of island structures that are irregularly distributed in the films with an average thickness of ~100 nm while the flat region between them has a thickness of 40 nm. This fact suggests that the films are growing in a Volmer-Weber growth mode, possibly due to there being greater cohesive energy between the atoms in the film, than between the atoms and the substrate [3]**.** The grey region next to the BTO-BFO film is an Au-Pd layer which was deposited to facilitate focused ion beam extraction. The Scanning Electron Microscopy (SEM) image on the right panel of Fig. 2, shows the surface structure of the sample, indicating island structures.

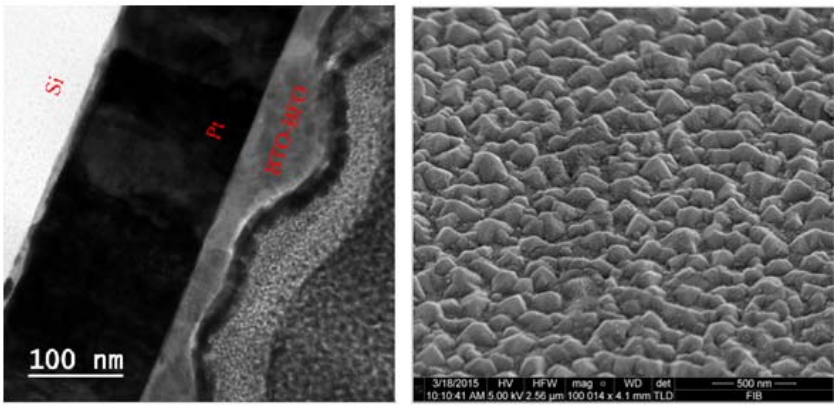

Fig. 2: Left panel: The cross sectional TEM of the BT-BFO film displaying the Si substrate, Pt wetting layer, island like BTO-BFO layer, and a layer of Au-Pd to facilitate focused ion beam extraction. Right panel: Top view SEM image of the BTO-BFO surface showing the island structures due to the Volmer-Weber growth mode of the BTO-BFO film. Both images were taken using a Jeol 4010 at 200 V.

2. EXPERIMENTAL RESULTS

2.1 Time Resolved Differential Transmission

For TRDR measurements, we employed a two color technique, with the pump wavelength of 400 nm (3.09 eV) between the bandgaps of BFO (2.67 eV) [4] and BTO (3.50 eV) [5], and the probe wavelength of 800 nm (1.55 eV) below both bandgaps. In Fig. 3, we show examples of the TRDR for two laser fluences: ~1μJ cm^{-2} and 3.8 mJ cm^{-2}. For the low fluence measurements, these pump-probe transients display a sharp initial increase in the reflectivity, followed by a fast recovery of ~3 ps, an ultimately a slower decay component which doesn't fully recover in the time scale longer than 25 ps. As shown in the inset, for the high fluence regime at room temperature, we see an opposite sign for the TRDR regime with a larger amplitude change (expected for a larger fluence regime), compared to the low fluence. For the fluence of 3.2 mJ cm^{-2}, a fast decay with a sub 10 ps decay time and a slower time scale, which doesn't fully recover at the time scale longer than 30 ps. In both cases, the longer time scales can be attributed to the lattice-carrier interaction where the photoexcited carriers can reach to equilibrium. Instead, the shorter time decay could correspond to an intermediate carrier time-dependent process [6,7].

Although the energy of the probe pulses is sub-bandgap, the TRDR can still be due to the complex refractive index associated with interband transitions. Excitation and subsequent phonon-mediated energy relaxation of carriers changes the occupation of electron and hole states which leads to fast variation of the complex refractive index [8]. Our fluence dependence dynamics demonstrate the importance of the initial electron-hole distribution density, switching the dynamics between photo-induced absorption to photo-induced reflectivity.

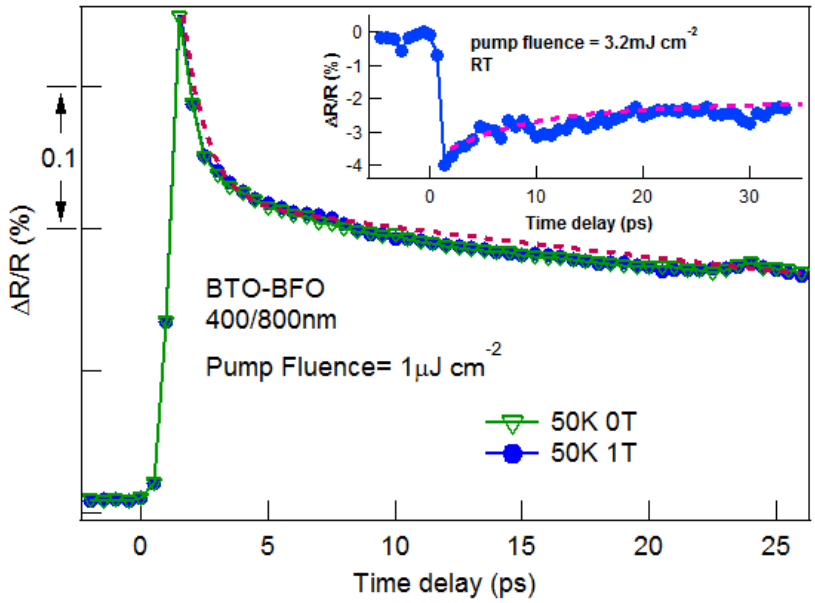

Fig. 3: Time resolved differential reflectivity (TRDR) of BTO-BFO, for a two-color (pump = 400 nm, Probe = 800 nm) scheme, at two different fluences. The low fluence regime shows smaller change of the TRDR and was observed only at low temperatures. The dynamic was not affected after applying an external field of 1 Tesla and has an opposite polarity, compared to the high fluence regime, presented in the inset. The fits are shifted for clarity.

2.2 Time Resolved Optically Induced Birefringence

We explored the transient birefringence by probing the changes in the polarization of the reflected probe pulses (ΔΘ), for the two different laser fluences, and Fig. 4 shows the examples of these measurements. For a fluence of 1μJ cm^{-2}, at zero time delay, we observed an initial sharp increase in ΔΘ, followed by a fast relaxation of ~ 2 ps and then a slower dynamic longer than 50 ps. We observe a smaller change in the TROIB in the low fluence regime compared to the high fluence case (presented in the inset). In addition, we observe a sign change of ΔΘ, for the high fluence regime, as shown

in the inset, which remains negative over the rest of the temporal range of our experimental setup (1.2 ns). The sign change occurs after ~800 ps; therefore it could be due to much slower processes than the changes in carrier distribution, for example dynamics of the electric polarization, resulting from photoexcited carrier recombination, heating in the lattice, and lattice vibrations.

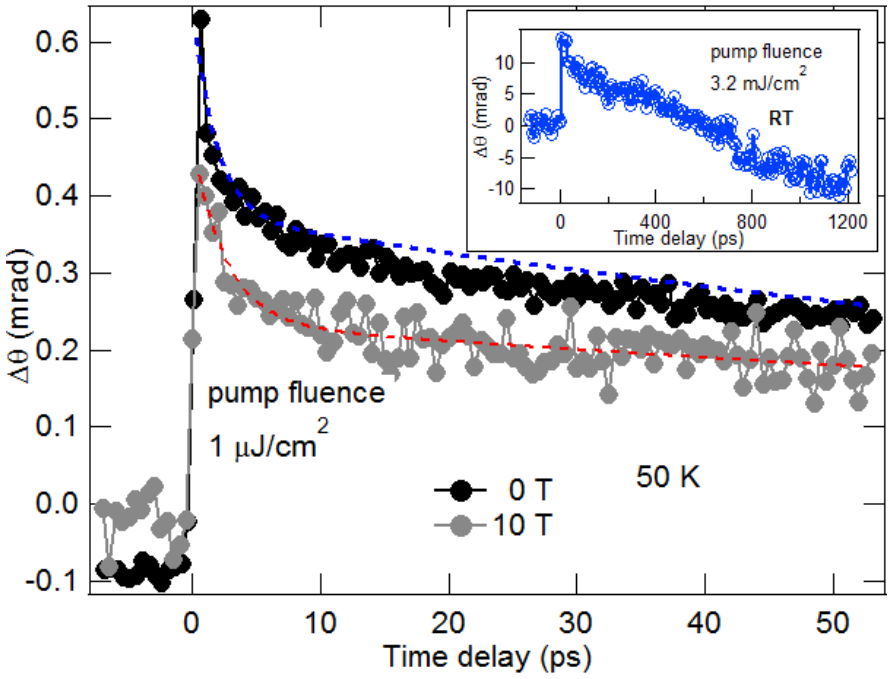

Fig. 4: The optically induced birefringence of the BT-BFO at two different laser fluences with 800 nm probe and 400 nm pump. The change in OIB is much smaller for a fluence of 1μJ cm^{-2} compared to the high fluence regime, presented in the inset. The time scale of the dynamic was not affected by the external magnetic fields up to 10 T. The fits are shifted for clarity.

3. CONCLUSION

In summary, we have observed several picosecond and nanosecond responses in our polycrystalline BTO-BFO film in two different optical pumping regimes. The TRDR and the TROIB we measured, both display a dependence on fluence, with the high fluence regime displaying sign changes, increased magnitude of response, and longer decay times. This result is complimentary of earlier observations of non-local order in polycrystalline BTO-BFO films [9]. Our results provide new insights on the time scales of the interactions in this, not yet extensively explored, material system. Our time resolved observations suggest that BTO-BFO could be used for applications such as optically driven switches, where the changes in the photo-excited carrier density can alter the dynamics.

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REFERENCES

1. S-C. Yang, A. Kumar, V. Petkov, and S. Priya "Room-temperature magnetoelectric coupling in single-phase $BaTiO_3$-$BiFeO_3$ system", J. App. Phys., 113, 144101 (2013).
2. T-J. Park, G. C. Papaefthymiou, A. J. Viescas, Y. Lee, H. Zhou, and S. S. Won. "Composition-dependent magnetic properties of $BiFeO_3$-$BaTiO_3$ solid solution nanostructures", Phys. Rev. B, 82, 024431 (2010).
3. A. J. Bell, F. Esat, T. P. Comyn "Microstructure development of $BiFeO_3$–$PbTiO_3$ films deposited by pulsed laser deposition on platinum substrates", Acta Materialia, 66, 44 (2014).
4. X. S. Xu, T. V. Brinzari, S. Lee, Y. H. Chu, L. W. Martin, A. Kumar, S. McGill, R. C. Rai, R. Ramesh, V. Gopalan, S. W. Cheong, and J. L. Musfeldt "Optical properties and magnetochromism in multiferroic $BiFeO_3$", Phys. Rev. B, 79, 134425 (2009).
5. P.C. Joshi and S.B. Desu "Structural, electrical, and optical studies on rapid thermally processed ferroelectric $BaTiO_3$ thin films prepared by metallo-organic solution deposition technique", Thin Solid Films, 300, 289 (1997).
6. Z. Jin, Y. Xu, Z. Zhang, G. Li, X. Lin, G. Ma, Z. Cheng, and X. Wang "Structural dependent ultrafast electron-phonon coupling in multiferroic $BiFeO_3$ films", App. Phys. Lett., 100, 071105 (2012).
7. Y. M. Sheu, S. A. Trugman, Y.-S. Park, S. Lee, H. T. Yi, S.-W. Cheong, Q. X. Jia, A. J. Taylor, and R. P. Prasankumar "Ultrafast carrier dynamics and radiative recombination in multiferroic $BiFeO_3$", App. Phys. Lett., 100, 242904 (2012).
8. M. Ulman, D. W. Bailey, L. H. Acioli, F. G. Vallee, C. J. Stanton, E. P. Ippen, and J. G. Fujimoto "Femtosecond tunable nonlinear absorption spectroscopy in $Al_{0.1}Ga_{0.9}As$", Physical Review B 47, 10267 (1993).
9. B. A. Magill, K-D Park, Y. Zhou, A. Chopra, Maurya, S. Priya, M. B. Raschke, A. Belyanin, C. J. Stanton, G. A. Khodaparast "Ultrafast Anisotropic Optical Response and Coherent Acoustic Phonon Generation in Polycrystalline BaTiO3-BiFeO3" (Unpublished).