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Ultrafast Photostriction in Thin Film Bismuth Ferrite and its Correlation to Electronic Dynamics

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ABSTRACT

A series of laser pump, x-ray probe experiments show that above band gap photoexcitation can generate a large out-of-plane strain in multiferroic $BiFeO_3$ thin films. The strain decays in a time scale that is the same as the photo-induced carriers measured in an optical transient absorption spectroscopy experiment. We attribute the strain to the piezoelectric effect due to screening of the depolarization field by laser induced carriers. A strong film thickness dependence of strain and carrier relaxation is also observed, revealing the role of the carrier transport in determining the structural and carrier dynamics in complex oxide thin films.

INTRODUCTION

Ultrafast lattice dynamics in an epitaxial thin film of the room-temperature multiferroic bismuth ferrite can be driven by ultrafast laser-generated photocarriers. We report a structural study of these dynamics with a temporal resolution of 100 ps. Multiferroics exhibit simultaneous magnetic and ferroelectric (FE) degrees of freedom [1, 2]. The coupling between these degrees of freedom and their interaction with mechanical and optical excitations is beginning to be understood under static conditions [3, 4], but the timescales of the interaction of polarization and

magnetism with strain and excited carriers are not yet known. Understanding these interactions is important to testing theoretical prediction of the coupling among strain, magnetism, and polarization as well as in eventual applications of multiferroics in electronics and optoelectronics.

We report a series of laser pump/synchrotron x-ray probe experiments performed at the 7ID beamline of the Advanced Photon Source (APS). The experiments reveal ultrafast variation of optically induced strain in epitaxial BFO thin film. Transient optical absorption spectroscopy shows close correlation between these structural changes and the dynamics of excited electrons.

EXPERIMENTAL DETAILS

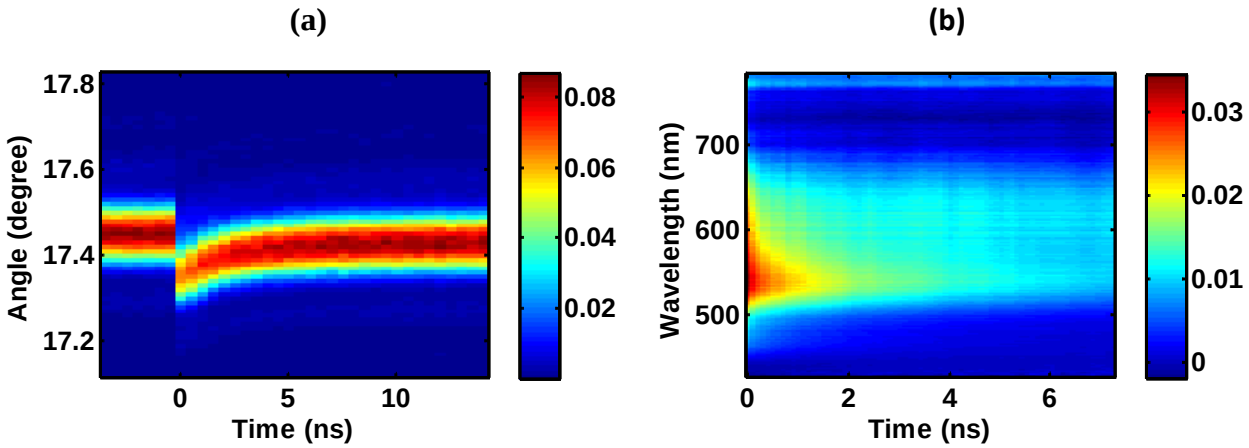

Fig. 1 (a) Shift of BFO 002 Bragg peak after the laser excitation, the color shows the relative intensity. (b) Transient absorption spectrum for an 88 ML BFO thin film, the color shows the optical density (OD).

X-ray scattering experiments were conducted in samples excited by optical pump pulses with durations of 50 fs and a wavelength of 400 nm. The optical photon energy was above the BFO band gap and resulted in the creation of carriers in an absorption depth of approximately 32 nm. The x-ray diffraction probe used x-rays with a photon energy of 10 keV and a duration of approximately 100 ps to probe the lattice dynamics at variable delays from the pump pulse. The BFO films had thicknesses of 10, 20, 50 and 88 monolayers (ML), prepared by molecular beam epitaxy on [001] $SrTiO_3$. These samples exhibit four twin FE domains, confirmed by the observation of the splitting of the pseudocubic 113 reflection peaks. The dynamics of the BFO layer were probed by studying the evolution of the intensity and wavevector of the 002 reflection. In the optical transient spectroscopy (TAS) measurement, performed at the Center for Nanoscale Materials, optical absorption in the wavelength range from 400 to 750 nm was probed by a chirped 1 ps white-light pulse at a variable delay after 400 nm pump pulse. The x-ray diffraction experiment measured the structural dynamics and the TAS measured the carrier dynamics.

DISCUSSION

Figure 1 (a) shows the time dependence of the intensity of the 002 Bragg reflection as a function the delay between the X-ray probe and the scattering Bragg angle. Figure 1(b) shows the transient absorption spectrum as a function of the interval between the pump and probe pulses. In Fig. 1(b), the rapid collapse of the absorption peak width at early times (< 1 ns) may indicates the loss of the carrier mobility as they cool down. The x-ray diffraction and TAS measurements exhibit similar nanosecond-timescale dynamics.

Figure 2 compares the strain measured from the angular shift of the Bragg reflection as a function of time with the time dependence of the optical density (OD) at 540 nm in the TAS measurement. The strain displays a fast rise occurring in a time less than 100 ps, followed by a decay characterized by two timescales. The characteristic time of the faster process depends on the laser fluence. The slower decay occurs over times longer than 10 ns and does not vary as a function of the laser fluence. The longer-time constant decay can be linked through a thermal model to the conduction of the optical heating of the lattice into the $SrTiO_3$ substrate. Thermal analysis by solving the thermal diffusing equation reproduces the experimental data across the full range of excitation conditions. The thermal model uses the coefficient of thermal expansion measured in these BFO thin films in a laboratory x-ray diffraction experiment, corrected for the case in which only the film is heated by using the Poisson ratio available in the literature [5]. The results of the model show that the heating effect contributes approximately 30% of the strain produced by optical excitation and well reproduces the experimental results [6].

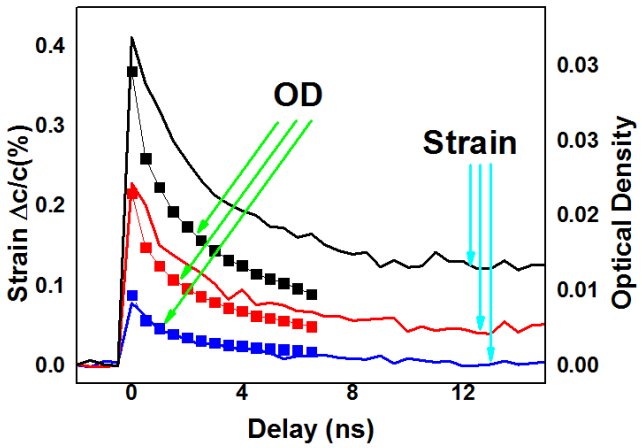

Fig. 2 Comparison of optical density (OD, points) and strain (lines) as a function of pump probe delay.

The strain in this regime is consistent with a mechanism in the depolarization field is screened by the photo-induced carriers. Based on a piezoelectric constant of 50 pm/V [1], the observed strain of 0.44% corresponds to a screened field of 880 kV/cm. A photostriction effect

with a smaller magnitude has been observed in BFO single crystals [7]. Similar effect is also reported in ferroelectric $PbTiO_3$ thin film [8]. The FE in BFO polarization is along the pseudocubic <111> directions, and as a result the increase of the out of plane lattice parameter leads to a rotation of the FE polarization in BFO and possibly the rotation of the AFM plane.

The peak magnitude of the strain is proportional to the laser fluence, as shown in Fig. 3(a). In addition, the angular width of the 002 Bragg reflection increases after laser excitation. The increased width following laser excitation is illustrated in the inset of Fig. 3(b). Figure 3(b), shows that the angular width of the x-ray depends on the fluence, with minimal changes at lower fluences and larger changes at higher fluences.

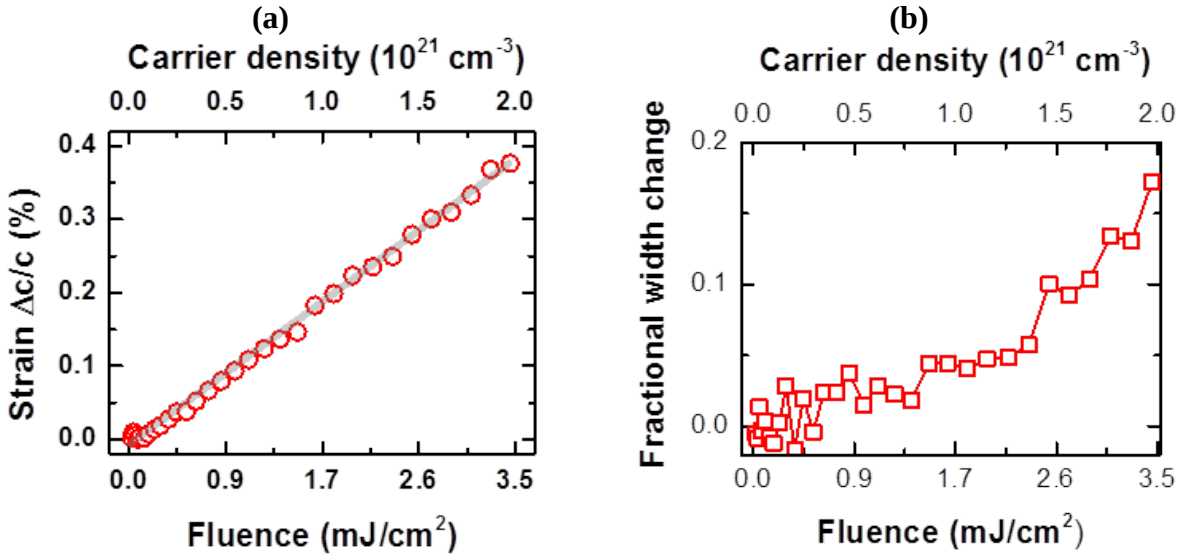

Fig. 3 (a) Magnitude of the peak strain as a function of the laser fluence. (b) Fractional change in the angular width of the 002 Bragg reflection as a function of the absorbed laser fluence.

The broadening of the diffraction peak can potentially arise from several effects. First, the formation of piezoelectric polarons [9] can occur by a process in which free carriers induce a local lattice distortion via the piezoelectric effect that in turn leads to a self-trapping of the carriers. The trapping or localization reduces the mobility of the carriers, consistent with the smaller than expected THz response of free carriers in BFO and the abrupt formation of absorption band in the TAS measurement in Fig. 1 (b), similar to observations in $LiNbO_3$ [10]. Localized lattice distortion due to polarons broadens reflection peaks and is observable when the broadening exceeds the angular width of the Bragg reflection, e.g. as in a manganite bilayer [11]. A second possible origin of the broadening is the introduction of gradient in the strain across the thickness of the BFO layer due to the modification of the internal polarization field by the presence of the carriers [12], which leads to localized inhomogeneous piezoelectric effect.

The carrier lifetime and strain relaxation time depend on the thickness of BFO layer, as shown in Fig. 4. At all thicknesses the strain relaxation time closely matches the time dependence of the TAS OD. We can estimate what timescale would be associated with the

dynamics of charge carriers in BFO by computing the time required for photoexcited carriers to travel across the thickness of the BFO layer. The results are consistent with a drift velocity on the order of ~10 m/s, and a timescale that is thus limited by the transport of excited carriers to recombination sites at the surface and buried BFO/$SrTiO_3$ interface. This slow drift time further supports the localized trapping model of the carrier in the thin film.

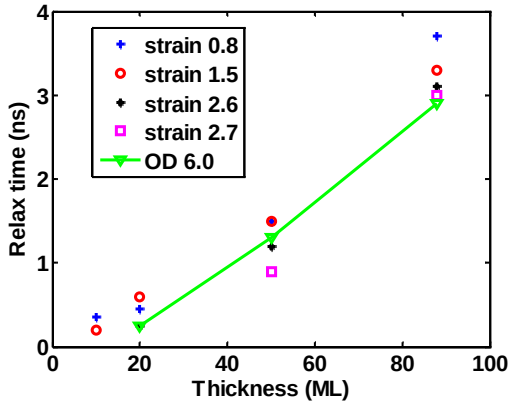

Fig. 4 Dependence of the carrier lifetime (derived from the time constant associated with the decay of the transient OD) and the strain relaxation time on the film thickness. The number in the legend indicates absorbed fluence in mJ/cm^2. The result indicate a carrier drift speed on the order of 10 m/s.

CONCLUSIONS

Our experiment reals the correlation of structural and electronic dynamics at a time scale relevant to application of BFO and similar material for application in electronic devices. It also opens the door for studying the real time, ultrafast electromagnetic coupling dynamics in multiferroics, a significant step beyond previous studies under static conditions [3, 4]. The thickness dependence of the structural and carrier dynamics also marks an important step towards understanding ultrafast carrier transport dynamics in such materials and the intimate coupling of the structure and the carrier dynamics.

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REFERENCES

1. G. Catlan and J. F. Scott, Advanced Mat. **21**, 2463 (2009).
2. J. Wang et al., Science **299**, 1719 (2003).
3. T. Zhao et al, Nat Mat. **5**, 823 (2006).
4. D. Lebeugle, et al., Phys. Rev. Lett. **100**, 227602 (2008).
5. S. Nakashima et al., J. Appl. Phys. **105**, 061617 (2009).
6. H. Wen et al., Phys. Rev. Lett., in press.
7. B. Kundys et al, Nat. Mat. **9**, 803 (2010).
8. D. Daranciang et al. Phys. Rev. Lett. **108**, 087601 (2012).
9. W.E. Tefft, Phys. Rev. **164**, 1032 (1967).
10. S. Sasamoto, et al, J. Appl. Phys. **105**, 083102 (2009).
11. L. Vasiliu-Doloc, et al., Phys. Rev. Lett. **83**, 4393 (1999).
12. V. Fiorentini et al., Phys. Rev. B **60**, 8849 (1999).