Measurement of transient photoabsorption and photocurrent of BiFeO₃ thin films: Evidence for long-lived trapped photocarriers

Author(s)
Yamada, Yasuhiro; Nakamura, Toru; Yasui, Shintaro; Funakubo, Hiroshi; Kanemitsu, Yoshihiko

Citation
Physical Review B (2014), 89(3)

Issue Date
2014-01-21

URL
http://hdl.handle.net/2433/180321

©2014 American Physical Society

Type
Journal Article

Textversion
publisher
Measurement of transient photoabsorption and photocurrent of BiFeO3 thin films: Evidence for long-lived trapped photocarriers

Yasuhiro Yamada, Toru Nakamura, Shintaro Yasui, Hiroshi Funakubo, and Yoshihiko Kanemitsu

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Midori-ku, Yokohama, 226-8502, Japan

(Received 29 October 2013; revised manuscript received 2 January 2014; published 21 January 2014)

We have studied the optical response and dynamical behavior of photocarriers in BiFeO3 thin films by means of transient absorption (TA) and photocurrent (PC) measurements. PC and absorption spectroscopy indicate that BiFeO3 thin films have an indirect band gap energy of ~2.4 eV. The TA and PC decay dynamics have fast (~1 ns) and slow (~100 ns) components that are attributed to the localization of free carriers to shallow trap states and the recombination of trapped carriers, respectively. The long decay time of the PC is caused by the thermal activation of trapped carriers into the conduction band. Long-lived trapped photocarriers can be linked to the ferroelectricity and give rise to unique photoinduced phenomena in BiFeO3.

DOI: 10.1103/PhysRevB.89.035133 PACS number(s): 78.47.jb, 77.55.fp, 78.47.db, 78.66.–w

I. INTRODUCTION

Transition-metal oxides have fascinating multifunctional properties that can be employed for a range of new device concepts, and the large remnant polarization, high Curie temperature, and strong multiferroic coupling of BiFeO3 makes this oxide one of the most promising device materials [1–4]. Bulk BiFeO3 crystals take a rhombohedrally distorted perovskite structure at room temperature, and the quasitetragonal phase in BiFeO3 thin films, which are usually deposited on SrTiO3 or DyScO3 substrates, is stabilized by the compressive strain induced by the lattice mismatch with the substrate [5]. Extensive studies of the dielectric properties of BiFeO3 and related heterostructures have been performed [6,7], and it has been reported that the tetragonal phase of BiFeO3 results in an enhancement of the spontaneous polarization [8,9].

The unique optical properties of BiFeO3 have also recently come under scrutiny; bulk BiFeO3 crystals exhibit a large photoinduced size expansion along the polarization direction [10,11], and a nonthermal, ultrafast piezoelectric response induced by above-band-gap photoexcitation has also been observed in time-resolved x-ray diffraction measurements [12]. These results imply that the photoexcited carriers (photocarriers) are strongly linked to the ferroelectric properties of BiFeO3. In addition, it has been reported that BiFeO3 thin films on DyScO3 display an above-band-gap photovoltage that is generated along the net polarization direction [13,14]. Photocarriers would thus appear to be driven by the ferroelectric depolarization field, which is the origin of the large photovoltaic effect. It has also been suggested that the photovoltaic properties of BiFeO3 are completely different from those of conventional photoconversion systems based on the built-in field of pn and Schottky junctions. The unique photoinduced phenomena observed in BiFeO3 may suggest new directions for ferroelectrics science and assist in the development of innovative ferroelectronics-based devices, including light-controlled elastic actuators and light-energy converters. However, the fundamental optical properties and photocarrier recombination processes of BiFeO3 that determine the exact optical response are still unclear. A study of the dynamical behavior of the photocarriers is thus essential for understanding the unique photoinduced effects in BiFeO3.

In this work, we report on the relaxation and recombination dynamics of photocarriers of BiFeO3 thin films investigated using a combination of transient absorption (TA) and time-resolved photocurrent (PC) measurements. The band gap energy was determined on the basis of the PC excitation spectrum to be approximately 2.4 eV, and the TA spectrum has a strong photoabsorption peak at around 2.3 eV, which we attribute to the optical transition of photoexcited electrons to the higher conduction band. The TA dynamics show two exponential decay components under weak photoexcitation, and we assign the fast component to the localization of free photocarriers and the slow decay component to the relaxation of photocarriers in the shallow trap states. These results are consistent with both the very fast decay of the PC signals, which mainly reflect the population of free photocarriers, and the thermal activation of the trapped carriers that gives rise to a long PC lifetime. Here, we discuss the photocarrier relaxation and recombination processes and their impact on the photoinduced phenomena in BiFeO3.

II. SAMPLE AND EXPERIMENTAL SETUP

BiFeO3 epitaxial thin films were fabricated by chemical vapor deposition [15]. Because the structural and ferroelectric properties of BiFeO3 thin films are dependent on the quality and crystal structure of the substrate, we fabricated thin films on two different substrates (SrTiO3 and DyScO3). The film thicknesses were 260 nm and 50 nm for the SrTiO3- and DyScO3-substrate samples, respectively. We measured the TA dynamics using femtosecond white-light pump–probe spectroscopy; pump and probe pulses with a delay time Δt were focused onto the sample surface, and the variation in the probe-pulse intensity induced by the pump excitation was detected as a function of Δt. The white-light probe pulses were generated by focusing a 1.2-eV laser pulse onto a sapphire plate. The pump energy was fixed at 3.1 eV. A wavelength-tunable femtosecond laser system based on a Yb:KGW...
Optical Density (arb. units) spectra of (a) BiFeO₃/SrTiO₃ and (b) BiFeO₃/DyScO₃. The insets are a guide for the eye. The transient sample surface, and femtosecond laser pulses (3.1 eV) were focused onto the gap between the electrodes [16]. The transient PC was recorded by an oscilloscope and a current–voltage converter. The time resolution of the PC measurement was about 6 ns.

III. RESULTS AND DISCUSSION

The band gap energy of BiFeO₃ has previously been reported to lie within a range of 2.4 to 2.8 eV, but optical absorption in the shallow trap states formed by defects and impurities smears the optical absorption edge that corresponds to the band gap energy, which makes it difficult to determine the exact band gap energy [17–20]. It has also been pointed out that the optical absorption peak due to a d–d transition appears in the near band-edge absorption spectrum of BiFeO₃ [19,20]. The optical absorption and PC spectra of BiFeO₃ thin films on the SrTiO₃ (BFO/STO) and DyScO₃ (BFO/DSO) substrates are shown in Fig. 1. The optical absorption spectrum of BFO/STO shows a significant increase above 2.4 eV, which is consistent with reported values of the band gap energy [20,21] and also has a long tail on the low-energy side. The BFO/DSO, however, shows no clear absorption edge around 2.4 eV, and the optical absorption below the band gap energy suggests that there is a high density of below band gap states introduced by defects due to the lattice mismatch. The onsets of the PC spectra (Fig. 1) of BFO/STO and BFO/DSO are approximately 2.3 and 2.4 eV, respectively. As the PC reflects the optical absorption that contributes to the PC generated by band-to-band photoexcitation, it is therefore less affected by the optical absorption of deep defect or impurity states. In other words, the PC is more sensitive to band-edge optical transitions. Tauc plots of the PC (insets in Fig. 1) reveal a linear variation in the PC of both BFO/STO and BFO/DSO, which is evidence of an indirect transition [22,23]. This assignment is consistent with our experimental results that show that almost no photoluminescence is observed from BiFeO₃ thin films even at low temperatures (data not shown) because most direct-gap semiconductors exhibit efficient light emission. The indirect gap and the band gap energy are also consistent with theoretical band calculations [21,24]. In an indirect-gap semiconductor, optical absorption involves wavenumber-conserving phonons, and we estimate \((E_g - \epsilon_{ph})\) to be 2.4 eV, where \(E_g\) and \(\epsilon_{ph}\) are the band gap energy and the phonon energy, respectively. As the phonon energy is typically much smaller than the band gap energy, we conclude that the band gap energy of the BiFeO₃ thin film is approximately 2.4 eV at 300 K.

![FIG. 1. (Color online) Optical absorption and PC excitation spectra of (a) BiFeO₃/SrTiO₃ and (b) BiFeO₃/DyScO₃. The insets show Tauc plots of the optical absorption and PC. The dashed lines are a guide for the eye.](image-url)
FIG. 2. (Color online) TA spectra of (a) BiFeO$_3$/SrTiO$_3$ and (b) BiFeO$_3$/DyScO$_3$ for different delay times. Dashed curves represent the two Gaussian functions that compose the 2.3-eV TA band. The inset illustrates the energy levels of BiFeO$_3$, respectively, as indicated by the arrows in the inset. The TA band crossover indicates that photocarriers in the band state relax to the shallow trap state.

The TA dynamics are shown in Fig. 3 for a probe energy of 2.3 eV (photoabsorption peak energy) and different excitation densities; the TA intensities were normalized at 200 ps. The TA decay profiles in the nanosecond time range, obtained from the cw-probe TA measurements, are shown in the inset. The TA intensity at 2.3 eV corresponds to the carrier density at the band state and shallow trap state. Between 0 and 200 ps, the TA decay profiles are dependent on the excitation density; a very fast decay component appears with an increase in the excitation density. This excitation-density-dependent decay component can be associated with Auger recombination involving three carriers under strong photoexcitation conditions [27,28].

Under weak photoexcitation fluence, the TA dynamics consist of fast and slow components. The lifetime of the fast component is about 1 ns in both samples, as determined by a single-exponential fitting over the range 0.2–2 ns. However, the slow component has a nonexponential decay profile. We obtained average slow lifetimes of 130 ns for BFO/STO and 160 ns for BFO/DSO by fitting a double exponential over the range 10–800 ns. Additional decay components with a longer decay time also exist, and these can be attributed to relaxation in the deeper states. Note that these very slow decay components are sensitive to the probe energy and focal position of the laser. We attribute the fast and slow decay components to the localization of free photocarriers and the relaxation of photocarriers in the shallow trap, respectively, as shown schematically in Fig. 4(a); according to our model, photoexcited electrons rapidly relax into shallow trap states (~1 ns) and reach thermal equilibrium, which is consistent with the nanosecond timescale of the TA crossover. These trapped carriers have a longer lifetime (~130–160 ns), and thermal activation of carriers in the shallow trap induces transitions to the conduction band that are reflected by the slow decay component.

To confirm our photocarrier recombination model described in Fig. 4(a), we examined the PC decay profiles of BFO/STO under different bias voltages [Fig. 4(b)]. It should be noted that we were careful in focusing the excitation laser onto the gap between the electrodes to avoid illuminating and heating the electrodes, which would induce a pyroelectric current independent of the bias voltage. The observed PC was very weak because of the large gap width needed to reduce the pyroelectric current. The PC increases linearly with the bias voltage, meaning that an ohmic contact is formed at the interface of the BiFeO$_3$ sample and electrodes. The PC decay profiles are almost independent of the bias voltage. Two decay components can be observed in the PC profiles: a very fast decay component that decays within ~6 ns (equivalent to the time resolution of the measurements) and a slow decay component with an estimated decay time of 200 ns (determined from a single-exponential fitting). The BFO/DSO sample showed similar PC decay dynamics, and the decay times were similar to those estimated from the TA results.

The logarithm of the time-integrated PC intensity as a function of inverse temperature [Fig. 4(b) inset] reveals a linear relationship that indicates the existence of a thermally activated process from the shallow trap state to the conduction band, which supports the recombination model proposed in Fig. 4(a). We found that the activation energies ($E_a$) of BFO/STO and BFO/DSO were 120 and 80 meV, respectively, based on an Arrhenius plot of the PC intensity; an activation energy of about 100 meV corresponds to the energy difference between the band state and shallow trap state, as well as being consistent with the energy shift of the photoabsorption peak (around
FIG. 3. (Color online) Normalized TA decay profiles of (a) BiFeO₃/SrTiO₃ and (b) BiFeO₃/DyScO₃ for different excitation densities. The inset shows the TA decay profiles in the submicrosecond time region and the calculated double-exponential function (blue curve).

FIG. 4. (Color online) (a) Schematic of the photocarrier relaxation and recombination processes in BiFeO₃. (b) PC dynamics of BiFeO₃/SrTiO₃ at different bias voltages (2, 4, 6, 8, and 10 V). The inset shows the time-integrated PC as a function of inverse temperature.
of free photocarriers is related to the very small PC observed in the photovoltaic measurements. While free photocarriers are rapidly trapped within 1 ns, trapped carriers are thermally activated and have an effectively long lifetime. We believe that our results provide a deep insight into the photoinduced phenomena in BiFeO₃.

ACKNOWLEDGMENTS

Part of this work was supported by The Sumitomo Electric Industries Group CSR Foundation, KAKENHI (No. 24740202 and No. 25247052), the Collaborative Research Program of Institute for Chemical Research, Kyoto University (No. 2011-6 and No. 2012-7), and JST-CREST.