Terahertz Radiation by an Ultrafast Spontaneous Polarization Modulation of Multiferroic $BiFeO_3$ Thin Films

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Terahertz (THz) radiation has been observed from multiferroic $BiFeO_3$ thin films via ultrafast modulation of spontaneous polarization upon carrier excitation with illumination of femtosecond laser pulses. The radiated THz pulses from $BiFeO_3$ thin films were clarified to directly reflect the spontaneous polarization state, giving rise to a memory effect in a unique style and enabling THz radiation even at zero-bias electric field. On the basis of our findings, we demonstrate potential approaches to ferroelectric nonvolatile random access memory with nondestructive readability and ferroelectric domain imaging microscopy using THz radiation as a sensitive probe.

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Ferroelectric oxides offer a wide range of functionalities demonstrating their potential for various electronic and photonic applications [1]. Among them, perovskite $BiFeO_3$ has attracted much attention for the presence of multiferroism at room temperature with simultaneous ferroelectricity and antiferromagnetism, as well as for the extremely large spontaneous polarization P_s observed in thin film form [2,3]. $BiFeO_3$ is a charge-transfer insulator exhibiting an energy gap of about 2.5 eV [4], which is quite small in contrast with the ordinary ferroelectrics whose energy gap generally lies in the ultraviolet region. Such distinction allows carrier excitation in $BiFeO_3$ with commercially available femtosecond laser pulses and, hence, enables us to develop ferroelectric ultrafast optoelectronic devices as widely demonstrated in semiconductors.

In this Letter, we report a novel terahertz (THz) radiation characteristic of multiferroic $BiFeO_3$ thin films triggered upon illumination of femtosecond laser pulses. Based on the bias electric field E_{bias} dependence of the THz amplitude, we show that the radiated THz pulse directly reflects the P_s state, indicating that THz radiation results from the ultrafast modulation of P_s of the $BiFeO_3$ thin films. This phenomenon can be applied universally to other ferroelectrics and provides new approaches to readout in nonvolatile random access memories and ferroelectric domain imaging systems.

THz radiation via illumination of femtosecond laser pulses provides considerable interest for versatile applications such as imaging for biomedical diagnosis and security, time-domain spectroscopy for material characterization, and a tool to evaluate the ultrafast dynamics of photoexcited charge carriers [5,6]. Intensive studies have, therefore, been carried out on THz radiation from photoconductive switches fabricated on various materials. The mechanism of THz radiation from a photoconductive switch is dominated by the dynamical motion of the free carriers created by laser illumination, in which the transient current surge developed within a subpicosecond time scale upon carrier excitation gives rise to electromagnetic radiation at THz frequencies. Through this approach, voltage-biased semiconductors have shown the best radiation efficiency among others, demonstrating their potential as a general THz radiation source [6]. On the other hand, transition metal oxides with perovskite structures have presented peculiar THz radiation characteristics originating from their strong electron correlations, as exemplified by the cases of high-transition-temperature cuprate superconductors [7] and colossal magnetoresistive manganites [8]. The present work on multiferroic $BiFeO_3$ thin films provides an alternate route to THz radiation based on this photoconductive approach.

200 nm-thick $BiFeO_3$ thin films with $(00l)$ orientation were grown on $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}(001)$ substrates, abbreviated as LSAT, by pulsed laser deposition with a KrF excimer laser at a growth condition of 800 °C for substrate temperature and 60 Pa for oxygen pressure. The ferroelectricity and the antiferromagnetism of the $BiFeO_3$ thin films at room temperature were confirmed by a ferroelectric tester and superconducting quantum interface device magnetometer, respectively. Photolithography and a sputtering method were used to fabricate a dipole-type photoconductive switch with Au electrodes on the surface of the $BiFeO_3$ thin film, which consists of a pair of 30 μm-wide strip lines separated by 20 μm with a dipole gap of 10 μm (Fig. 1).

In Fig. 1(a), we present the schematic illustration of THz radiation from a photoconductive switch fabricated on a $BiFeO_3$ thin film. Generation of a single-cycle THz pulse propagating into free space was achieved by carrier excitation upon illumination of femtosecond laser pulses with a center wavelength λ of 400 nm. We used the second harmonic of a mode-locked Ti:sapphire laser with λ of

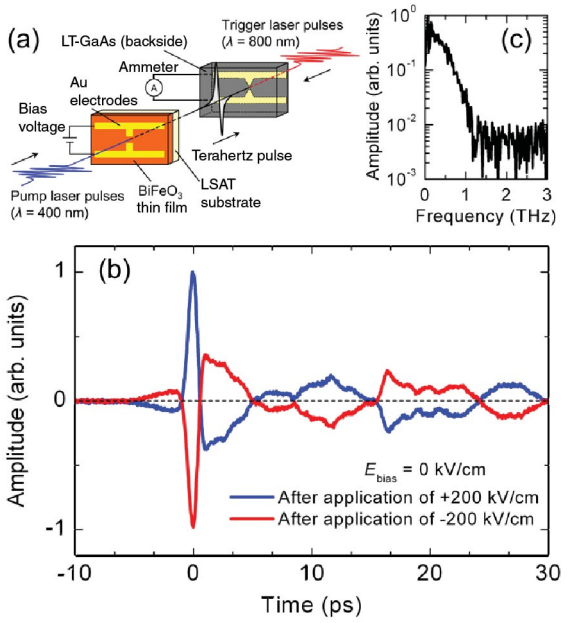

FIG. 1 (color). (a) Schematic of THz radiation and detection. (b) Time-domain waveform of the THz pulse radiated from the $BiFeO_3$ photoconductive switch measured at a zero-bias electric field after applying a bias electric field E_{bias} of ± 200 kV/cm. The dashed line represents the zero-level line shown for clarity. (c) Fourier transformed amplitude spectrum of the waveforms in (b).

800 nm, repetition rate of 82 MHz, and pulse duration of 100 fs, which was generated through a BaB_2O_4 nonlinear crystal. The laser power at λ of 400 nm was fixed at 5.5 mW and focused to a spot diameter of 20 μm. The radiated THz pulses from $BiFeO_3$ thin films were focused onto a bow-tie-type low-temperature-grown GaAs (LT-GaAs) photoconductive detector. The laser pulse at λ of 800 nm was partly split by a beam splitter and introduced to the other side of the LT-GaAs detector after a time delay [Fig. 1(a)]. A photocurrent I_{photo} is instantaneously produced in LT-GaAs when hit by both the trigger pulse and the THz pulse. Since I_{photo} depends on the electric field of THz radiation, the time-domain waveform of the THz pulse (both the amplitude and the phase) can be obtained by varying the optical delay line of the laser pulse and measuring the corresponding change of I_{photo} (photoconductive sampling technique) [6]. All measurements were performed at room temperature.

Figure 1(b) shows a typical example of two time-domain THz waveforms radiated from the $BiFeO_3$ photoconductive switch at E_{bias} of 0 kV/cm, measured after once applying E_{bias} of ± 200 kV/cm. The two THz waveforms measured under the same condition, but with different initial treatment, are nearly identical, both consisting of a single-cycle pulse centered at 0 ps with a pulse width of about 0.84 ps, except that they have a reversed phase by π with one another. This definitely represents a ferroelectric peculiarity of a memory effect. Accordingly, the two waveforms show an identical Fourier transformed amplitude spectrum exhibiting a frequency component extending up to 1 THz [Fig. 1(c)]. For standard comparison, we also measured the THz radiation characteristics of LT-GaAs, which is a well-known reference sample [6]. In the same condition, but with E_{bias} of 10 kV/cm applied, the amplitude of THz radiation in LT-GaAs was about 20 times larger than that of $BiFeO_3$. The pulse width was also estimated to be about 2 ps for LT-GaAs, slightly broader compared to the one in $BiFeO_3$ ($\sim$0.84 ps). These differences presumably arise from the different carrier mobility and scattering rate of the two materials.

Followed by the main THz pulse, a broad oscillatory feature is noticeable in Fig. 1(b). Intrinsic oscillation in THz waveforms is known to appear due to excitations of a phonon polariton or optical phonon modes [6]. However, these can be ruled out since probing of phonon-polariton beats requires an extremely high intensity of the laser pulses (several orders of magnitude larger than the one used here), and no optical phonon modes exist in such a low frequency ($\sim$60 GHz). We further note that structures due to water absorption and multiple reflection of the THz pulse at the film-substrate interface also need to be considered, which can be seen in the amplitude spectrum in Fig. 1(c). The specific origin of the oscillatory feature is obscure at the moment, and more references on nonequi-

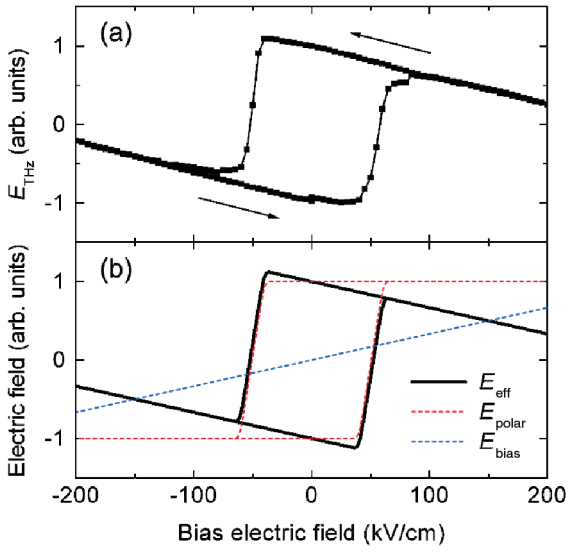

FIG. 2 (color). (a) Main peak amplitude of the THz pulse E_{THz} radiated from the $BiFeO_3$ photoconductive switch as a function of the applied bias electric field. The arrows indicate the sequential directions. (b) An ideal model of the macroscopic electric field induced to a pair of electrodes in typical ferroelectrics for understanding the tilted hysteresis loop in (a). E_{eff}, E_{polar}, and E_{bias} represents the effective electric field induced between the electrodes, the electric field derived by electric polarization, and the applied bias electric field, respectively. E_{eff} is expressed by $E_{polar} - E_{bias}$.

librium dynamics in ferroelectrics along with other experiments such as pump-probe spectroscopy are indispensable for its deep understanding. In the present Letter, we focus on the main THz pulse and devote our discussions to its intriguing features.

Noncentrosymmetric materials can produce THz radiation through a second-order nonlinear optical effect when they satisfy a severe phase-matching condition under the incidence of high-intensity laser pulses in the transparent region [9,10]. Taking account of this matter, we examined the response of $BiFeO_3$ thin films to the illumination of laser pulses at λ of 800 nm, which show negligible absorption in $BiFeO_3$ [4]. Despite the high laser power of 180 mW illuminated onto the film, which was about 30 times larger than the case at λ of 400 nm, THz radiation was not observed in such a situation. This indicates that the THz radiation presented in Fig. 1(b) is definitely triggered by the photoexcited charge carriers and not by the nonlinear optical effect.

In order to achieve a further insight, we measured the main peak amplitude of the THz pulse E_{THz} as a function of E_{bias} [Fig. 2(a)]. In the photoconductive switches reported so far [6], which are all nonferroelectric, E_{THz} generally has a linear relationship with the applied E_{bias} reversing its phase by π when the polarity of E_{bias} is changed, without showing any hysteresis. However, in the case of $BiFeO_3$, we observed a clear hysteresis loop [Fig. 2(a)], which looks familiar with the common electric polarization hysteresis loop observed in ferroelectrics except for the slight tilted shape where the intensity of E_{THz} is suppressed at high E_{bias}. We explain such a hysteresis loop by considering the macroscopic electric field biased to a pair of electrodes in typical ferroelectrics [Fig. 2(b)]. The effective macroscopic electric field E_{eff} induced to a pair of electrodes is ideally expressed by $E_{\mathrm{eff}} = E_{\mathrm{polar}} - E_{\mathrm{bias}}$, where E_{polar} represents the electric field derived from electric polarization ($= P/\epsilon_0$; P: electric polarization and ϵ_0: electric constant). Because of the screening of E_{polar} by E_{bias}, E_{eff} is suppressed at high E_{bias} and shows a tilted hysteresis loop in analogy with the E_{THz} loop observed in Fig. 2(a).

These features show the direct relationship of THz radiation with P_s, which emerges as a result of ultrafast P_s modulation introduced by the mobile photoexcited charge carriers. Namely, upon illumination of a single laser pulse, the accumulated charges associated with P_s become partially discharged instantaneously due to the screening by the photoexcited carriers. This modulation of P_s gives rise to THz radiation via dipole radiation according to classical electrodynamics. Beneath the static electric field formed by the surrounding dipole moments, the excited carriers immediately relax to form the original ferroelectric state. We assume that the ferroelectric ordering is not persistently disarranged upon photoexcitation here, because only a small number of photons is injected into the film compared to the total number of the unit cell covered by the laser spot; i.e., the number of injected photons per cubic centimeter is considered to be of the order of 10^{17} per pulse, whereas the number of the perovskite unit cells per cubic centimeter extends up to the order of 10^{22}.

Such characteristics open a way to a variety of applications using THz radiation as a sensitive probe. The hysteretic feature demonstrates the potential of ferroelectric photoconductive devices to act as nonvolatile random access memories, where the writing will be performed by the application of E_{bias} and the reading by detecting THz radiation. This is accomplished by laser illumination and the "0," "1" information is determined by the signs of E_{THz}, whether positive or negative. To express the switching operation, the temporal change of E_{THz} with varying E_{bias} is shown in Fig. 3(a). The application of positive E_{bias} of $+200$ kV/cm [Fig. 3(b)] writes down information which is sustained even after the removal of E_{bias}. THz radiation is indeed detected only when the laser is illuminated onto the film. In turn, the application of an opposite E_{bias} of -200 kV/cm erases the previous information and writes down new information to the film. We confirmed that the written information was sustained for more than two weeks in the absence of E_{bias}. Since the "on" and "off" operation of laser illumination does not induce a change of the P_s state, this process can be regarded as a nondestructive readout.

With THz radiation exhibiting a direct relationship with P_s, scanning of the two-dimensional distribution of E_{THz} allows us to visualize the ferroelectric domain structures by distinguishing the orientation of the 180° domains from the signs of E_{THz}. For demonstration, we applied this imaging technique to two different types of ferroelectric domain structures, which were realized by changing the poling conditions. In Fig. 4, we show four domain images of a section of the $BiFeO_3$ thin film at zero-bias electric field after poling the film with a bias voltage V_{bias} of ± 200 V

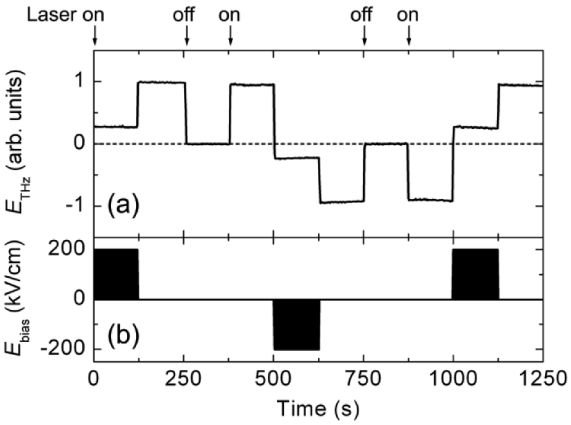

FIG. 3. Switching operation of the $BiFeO_3$ photoconductive switch as a function of time probing with THz radiation. Temporal change of (a) THz amplitude E_{THz} and (b) the applied bias electric field E_{bias}. The dashed line represents the zero-level line shown for clarity.

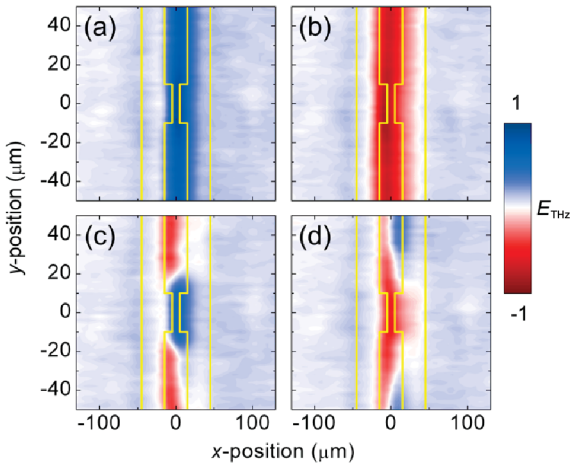

FIG. 4 (color). Visualization of 180° ferroelectric domain structure of the $BiFeO_3$ thin film probing with THz amplitude E_{THz}. Domain structure after poling the film with a bias voltage V_{bias} of (a) +200 V and (b) −200 V with simultaneous laser illumination, and domain structure after poling with V_{bias} of (c) +200 V and (d) −200 V without laser illumination. The application of V_{bias} of ±200 V corresponds to applying an electric field of ±200 kV/cm in the region between the dipole gap (the distance between the electrodes is inhomogeneous). The geometry of the Au electrodes is also shown by the yellow line in the respective images. Opposite 180° ferroelectric domains are distinguished by the blue and red colors based on the sign of E_{THz}.

with [Figs. 4(a) and 4(b)] and without [Figs. 4(c) and 4(d)] simultaneous laser illumination. The initial poling treatment of "applying V_{bias} of ±200 V with simultaneous laser illumination" is performed by once scanning the objective area at ±200 V. This treatment was also carried out prior to the measurement in Figs. 4(c) and 4(d). Thus, the former state before the poling treatment of Fig. 4(c) [Fig. 4(d)] corresponds to the image shown in Fig. 4(b) [Fig. 4(a)]. Domains with opposite polarization states appear as blue and red areas, depending on the sign of E_{THz}. By comparing the images of each single pair [between Figs. 4(a) and 4(b), as well as Figs. 4(c) and 4(d)], one can see that only the domains between the electrodes have changed their states by the application of opposite V_{bias}, while the other areas are independent of V_{bias} and remain unchanged. The different poling treatment, whether V_{bias} was applied with or without laser illumination, gave rise to an interesting feature as demonstrated by the comparison of the pair of Figs. 4(a) and 4(b) by the pair of Figs. 4(c) and 4(d). In Figs. 4(a) and 4(b), the entire domains between the electrodes have managed to reverse their phase by π. On the contrary, in Figs. 4(c) and 4(d), only the area near the dipole gap has reversed its domains where maximum electric field is applied due to geometric effect, while the other area between the two strip lines has not, realizing the coexistence of two opposite 180° domains aligned side by side between the electrodes. The origin of the two different states can simply be understood by the term "photoassisted P_s switching" previously reported in $BaTiO_3$ [11] and $Pb(Zr, Ti)O_3$ [12] thin films, where the combination of ultraviolet light exposure with applying V_{bias} showed superior switching ability than the application of V_{bias} alone. Since the spatial resolution of this imaging technique is limited by the diameter of the focused laser spot, we assume that a more detailed domain structure can be observed by focusing the laser spot down to a submicrometer scale. This guarantees the potential of the present technique to compete evenly with the other fascinating ferroelectric domain imaging tools such as atomic force microscopy [13] and x-ray microdiffraction [14].

In conclusion, we have demonstrated a novel THz radiation functionality of a multiferroic $BiFeO_3$ thin film triggered via ultrafast modulation of P_s upon carrier excitation by the illumination of femtosecond laser pulses. The present phenomenon provides potential approaches to nondestructive readout in nonvolatile ferroelectric memory as well as a 180° ferroelectric domain imaging system. Since $BiFeO_3$ belongs to a class of multiferroics, measurement under magnetic field is promising, for it may give rise to an additional degree of freedom in the THz radiation feature also providing an additional functionality in device designing.

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