The propagation effects in ultrafast nonlinear electro-optical modulation in thin film on a substrate

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Abstract. The propagation of short optical and terahertz pulses through a noncentrosymmetric (ferroelectric) film on a centrosymmetric substrate is considered. The effect of terahertz electro-induced second harmonic generation is observed in the film. It is shown that the difference in the group velocities of THz and optical pulses leads to a non-mirror-like dependence of the transient nonlinear-optical response upon a mirror image of the film–substrate structure relative to its surface.

1. Introduction
Presently, table-top sources of terahertz radiation (THz) provide ultrashort pulses with 1 ps duration and peak amplitude up to several MV/cm. Such single-period pulses can be used as a unique means for all-optical ultrafast control of the material properties by the electric field of these pulses. The effects of ultrafast THz modulation of the sample properties are studied by a “pump–probe” technique, in which THz pulse is used as a pump, and a femtosecond optical pulse is used as a probe. The rotation of the optical polarization due to the birefringence under the action of the electric field of the terahertz pulse [1–3] and second harmonic generation (SHG) [4–8] are possible effects for detection.

When interpreting the results of observations, problems arise related to the effects of the propagation of a terahertz pulse in a medium: echo effects [9], interference effects [10], phase change effect as a function of the thickness of the medium [11], etc.

Propagation problems are of crucial importance to interpret the data, and must be taken into account for a full description of the interaction of terahertz radiation with matter.

Presently, interaction of strong single period THz pulse have been studied with several types of materials. It includes semiconductors [12–14], magnetics [15, 16], and ferroelectrics [17, 18]. While in semiconductors electrons are completely responsible for the observed electro-optical effects, in magnetics and ferroelectrics, corresponding order parameters may play important role in THz pulse-matter interaction. The ability to control order parameter on ultrafast timescale has been an unattainable goal for the researchers for a long time, which makes solving of the problem of great importance.

Conventional measurement techniques, both magnetic and electric are usually limited to a few megahertz and do not allow sub-100-picosecond time resolution. In the same time the
intra-atomic response to external fields may occur orders of magnitude faster [19, 20]. In [5], we showed that interaction of a terahertz pulse with a ferroelectric thin film BaSrTiO$_3$ results in a partial $90^\circ$ switching of dielectric polarization at a time scale comparable with a soft mode reverse frequency.

In this paper, we study the effects on a time scale much longer than THz pulse duration. The same system, ferroelectric thin film on a substrate is studied. Optical second harmonic generation is used as a measure of perturbation of electronic and ionic subsystems. Nonlinear optical response of the system was simulated with phenomenological model which takes into account dispersion of terahertz and optical pulses.

2. Experimental setup

We have performed two types of experiments. The main measuring scheme was terahertz pump–optical probe spectroscopy. Additionally, terahertz time-domain spectroscopy (THz-TDS) was used to characterize THz pulse. The experimental setups are shown in figure 1(a). These two schemes have a common part as well. In both setups the radiation of the chrome-forsterite laser system with pulse energy of 2 mJ, a wavelength of 1240 nm, duration of 100 fs at a pulse repetition frequency of 100 Hz, was divided into two beams: optical pump and optical probe.

Terahertz radiation was generated by optical rectification of femtosecond pulses (optical pump pulse) in a commercially available nonlinear organic crystal OH1: 2-(3-(4-Hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile. For a wavelength of 1240 nm, the efficiency of the nonlinear-optical conversion in this material takes the maximum value due to excellent velocity matching between THz and optical pump wavelengths [21]. To collimate and focus terahertz radiation, parabolic mirrors were used. The focal lengths of the mirrors were chosen to provide the smallest spot diameter in the beam waist with full width at half maximum of THz pulse about of 800 $\mu$m.

Infrared probe was spatially and temporally overlap on a sample (for THz-pump–optical probe) or electro-optical crystal (for THz-TDS) with THz pump. The beam size of the probing
radiation was 50 \( \mu m \), which is much smaller than the THz beam size. In this case, we can assume that the sample is probed in a region with a spatially uniform THz electric field. The time delay between the THz pump and the ir pulses was controlled by changing the path length of the ir pulse by an optical delay line.

In terahertz pump–optical probe spectroscopy, the second optical harmonic at a wavelength of 620 nm, generated by a femtosecond optical pulse at a wavelength of 1240 nm from the sample, was recorded by a photomultiplier (PMT) with a band-pass interference filter at a wavelength of 620 \( \pm 10 \) nm at the optical input. The signal measurement time for each delay time was 1 s. To increase signal-to-noise ratio, the measurement was recorded 10 times. Since the pulse duration from the PMT is about of several nanoseconds and the repetition rate of laser pulse is 100 Hz, the possibility of using the synchronous technique to record nonlinear optical response is difficult due to high duty cycle. In our setup the signal from the PMT was registered by oscilloscope and processed using LabView software. The direction of polarization THz radiation was fixed horizontally in the laboratory coordinate system.

In the time domain spectroscopy, the method of electro-optical detection was used [22]. The THz pulse was focused by parabolic mirrors onto an electro-optical GaP crystal. Terahertz induced changes of the birefringence in the GaP is proportional to the amplitude of the electric field (similarly to the Pockels effect). The THz-induced birefringence can be regarded as the ellipticity of the polarization of the optical pulse due to the interaction with the crystal GaP. The induced ellipticity was detected by a femtosecond pulse at a wavelength of 1240 nm. A balanced detector was used to measure ellipticity and, consequently, the electric field amplitude. In contrast to the methods described in [23, 24], this approach requires calibration. Power calibration of the terahertz signal was carried out by the Golay cell. The electric field was calculated by the method described in [21]. The maximum electric field of the THz pulse was 1 MV/cm.

The angle of incidence of terahertz and optical pulse was 0\(^{\circ}\) for the both setups. Transmission geometry of the experiments was used. All measurements were carried out at room temperature and dry atmosphere. Humidity was monitored by a hygrometer and was less than 2%.

3. Sample

The 400 nm (Ba\(_{0.8}\)Sr\(_{0.2}\))TiO\(_3\) (BST) epitaxial film was fabricated by radio-frequency sputtering on the 600 \( \mu m \) MgO (001) substrate. For such composition the film is in ferroelectric phase at room temperature [25].

In the optical scheme, the BST–MgO sample was set in such a way that the electric field of the terahertz wave was parallel to one of the crystallographic axes of the film and substrate.

The measurements were carried out with two orientations of the BST sample: the BST film or substrate were faced to THz and optical pulses (figure 2).

4. Results and discussion

The incident THz pulse and THz time-domain profiles transmitted through the BST film are shown in figure 1(b). For the time delay from –1 to 1 ps, these two profiles are identical showing unchanged THz pulse after its propagation through the BST–MgO sample. However, for much longer time delay at \( \tau_d = 12.5 \) ps additional pulse appeared for BST–MgO sample.

The position of this pulse agrees well with the calculated value of the optical path passed by the terahertz pulse after reflection from the back surface of the substrate:

\[
\tau_d = \frac{2L_{gr,MgO}}{c},
\]

where \( c \) is speed of light; \( n_{gr,THz}^{MgO} \) is refractive index for group velocity of THz pulse. Here we have to mention that for 1.5 THz, which corresponds to a middle frequency of THz pulse, dispersion
Figure 2. Dependences of the second harmonic intensity on the delay time between terahertz and optical pulses for a BST film on a substrate. The thin, thick and dashed arrows correspond to THz, the optical drop and the optical pulse at the second harmonic pulse, respectively.

of MgO tends to zero. In this case group velocity equals phase velocity, and ordinary refractive index can be taken as refractive index for group velocity. Thus, \( n_{\text{MgO}}^{\text{THz}} = 3.11 \) according to [26].

SHG dependencies upon the time delay between THz and optical pulses are shown in figure 2. These curves have peculiarities at \( t_{d1} = 0 \) ps and \( t_{d2} = 12.5 \) ps for BST–MgO (identically to TDS measurements).

Additionally, a strong peculiarity at \( t_{d} = 3 \) ps appears for both geometries. This value of time delay does not agree with the expected equidistant position between \( t_{d1} \) and \( t_{d2} \) (which we would call mirror-like). Thus, the dependence which we observed we call a non-mirror-like dependence on time delay regarding to the sample surfaces.

For interpretation of the obtained experimental results we performed a simulation of the nonlinear-optical response of the samples under consideration.

Let us find a temporal dependence of correlation function for terahertz and optical pulses. The correlation function depends on the time delay. Pulses go through the centrosymmetric substrate with the thickness \( L \) and both surface of the sample are the sources of SHG: one of it is BST film with effective thickness \( d_1 \ll L \), another one is back surface of the sample (substrate) with effective thickness \( d_2 \ll L \). Thus, the propagation factor is significant only in the substrate.

The optical and THz pulses pass through the medium with the variant time due to difference in the group velocity. Hence, their mutual arrangement changes.

The electric field of the optical pulse is given by the Gaussian distribution:

\[
E_{\text{opt}}(t) = \frac{A}{\sqrt{2\pi} \tau_{\text{opt}}} \exp \left[ -\frac{(t - t_{\text{opt}}^0)^2}{2\tau_{\text{opt}}^2} \right],
\]

where \( \tau_{\text{opt}} \) is pulse duration, \( t_{\text{opt}}^0 \) is pulse position in time space.

We assume the electrical field profile of THz pulse is sum of Gauss distributions with different amplitude and central position shifted to the left and right from the central peak:

\[
E_{\text{THz}}(t, \tau) = G(A, 0) + G(B, t_1) + G(C, -t_1),
\]
Figure 3. (a) Model curve for THz and optical overlap as instantaneous correlation functions on the front and back surface of the sample; (b) dependence of the SHG on the time delay between terahertz and optical pulses; (c) envelope of the correlation function during the transmission of pulses from the front and back surfaces of the sample.

where

\[ G(F; t_{\text{offset}}) = F \exp \left[ -\frac{(t - t_0(t) + t_{\text{offset}})^2}{2\tau_{\text{THz}}^2} \right] \]  

is Gauss distribution with amplitude \( F \) and central position shifted from the central peak by the value \( t_{\text{offset}} \) and

\[ t_0(t) = t_0^{\text{THz}}(\tau) + n_{\text{THz}}^n t_{\text{opt}} \]  

is the THz pulse temporal position taking in account the difference in the refractive indices and time delay between THz and optical pulses, \( n_{\text{opt}} = 1.71 \) is optical refractive index for substrate at \( \lambda = 1240 \) nm. Qualitatively, the temporal profile of such pulse (figure 3) coincides with the real THz pulse [see figure 1(b)]. The correlation functions of THz and optical pulses for each surface is given by

\[ A_{\text{cor1}}(\tau) = \langle E_{\text{opt}} \otimes E_{\text{THz}} \rangle(t, \tau) = \int_{-L-d_1/2}^{L+d_1/2} E_{\text{THz}}(t - \xi, \tau) E_{\text{opt}}(\xi) d\xi, \]

\[ A_{\text{cor2}}(\tau) = \langle E_{\text{opt}} \otimes E_{\text{THz}} \rangle(t, \tau) = \int_{L/2-d_2/2}^{L/2+d_2/2} E_{\text{THz}}(t - \xi, \tau) E_{\text{opt}}(\xi) d\xi, \]

where \( \otimes \) is the convolution symbol and the integration takes place in regions corresponding to the thickness of the front and back surfaces \( d_1 \) and \( d_2 \), respectively.

THz electrical field induced electro-dipole nonlinear polarization on the second harmonic wavelength can be determined as

\[ P_1(\tau) \propto \chi_{\text{film}}^{(3)} A_{\text{cor1}}(\tau), \quad P_2(\tau) \propto \chi_{\text{surf}}^{(3)} A_{\text{cor2}}(\tau), \]

where \( \chi_{\text{film}}^{(3)} \) is nonlinear susceptibility of film, \( \chi_{\text{surf}}^{(3)} \) is nonlinear susceptibility of the surface. The last one is determined in a classic form [27, 28].

Thus, temporal dependence of second harmonic signal on the time delay between pulses registered by detector is given by

\[ I_{2\omega}(\tau) \propto |P_1(\tau) + P_2(\tau)|^2. \]
As shown in figure 3, the SHG from the front surface has maximum at the zero time delay (temporal overlap position). Same nonlinear response appears at the time delay 12 ps, when THz and optical pulses occur on the front surface again after THz round-trip reflection.

A nonlinear optical response from the back surface appears during a delay that does not correspond to the travel time of one pulse, but is defined as the difference in the pulse path. It should be noted this peculiarity is due to time-integrated method of registration.

The detection system (PMT) is in standby mode for each position of the delay line and records any (all) photons that occurred during the integration time (1 s). Therefore, the terahertz and optical pulses are located inside the substrate at some intermediate time (not at the source of SHG). However, they move toward the source of the SHG on the back surface of the sample and overlap in it, because the optical pulse overtakes the terahertz pulse. This phenomenon gives significant changes in the SHG signal at the “wrong” time delay (2.5 ps).

We also note that in the case when the condition $d_2 \ll L$ is satisfied, the shape of the SHG pulse coincides with the square of the THz electric field profile.

5. Conclusions

We have shown the effect of the difference in the group velocities of the terahertz and optical pulses on the transient dependencies of the electric field induced second harmonic generation.

In the case of matching the speed, the SHG signal from the back surface of the sample is strictly determined by the optical paths that transmit optical and terahertz pulses. The SHG signal from the back surface is located halfway between the SHG signal from the front surface and its round-trip reflection.

When dispersion is taken into account, the temporal position of the SHG signal from the back surface is determined by the ratio of the refractive indices between THz and optical pulses and shifted from the middle towards the smaller values of the time delay. Asymmetry (non-mirror) nonlinear optical response is observed.

We proposed a model for calculating the nonlinear transient dependencies, which is applicable for a noncentrosymmetric film on a centrosymmetric substrate. The method is based on the convolution of temporal forms of terahertz and optical pulses on nonlinear sources.

Our findings are important for interpreting the results of diagnostics of layered structures by the second harmonic generation method.

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