Broadband and gap-free response of a terahertz system based on a poled polymer emitter-sensor pair

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We present a terahertz (THz) system based on a poled electro-optic (EO) polymer emitter-sensor pair for the generation and detection of broadband electromagnetic pulses free of spectral gaps. The gap-free THz spectrum obtained from the system is attributed to the amorphous form of the EO polymer films. Using ~50-fs laser pulses centered at ~800 nm, a ~100-μm thick emitter, and a ~180-μm thick sensor, the observable bandwidth is ~12 THz. We also present an experimental study, in a systematic manner, on the effect of phase mismatch in the polymer emitter-sensor pair.
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Using ultrashort laser pulses to generate and detect pulsed broadband terahertz (THz) radiation has been under intensive investigation for the past two decades.[1–9] Its advancement has led to the development of some important techniques such as THz time-domain spectroscopy (THz-TDS),[10] optical-pump/THz-probe,[11] and THz imaging and tomography,[12] which have been widely used for fundamental materials studies, as well as applications in medical and biological science. In general, either an optoelectronic approach associated with radiating photoconductive (PC) antennae[1,2] or an optical approach associated with nonlinear electro-optic (EO) materials[4–8,11,13–15] is employed to generate pulsed broadband THz waves. Similarly, for the THz detection, either PC sampling,[1,2,9] an optoelectronic approach, or free-space EO sampling,[5–8,11,13–15] an optical approach, is usually employed. Until very recently, optoelectronic THz systems based on semiconductor PC elements provided useful bandwidth, without postexperimental data reconstruction, of only a few THz, which was claimed to be limited by the photoconductor carrier lifetime. Shen *et al.* reported the first optoelectronic THz system, with a 15-fs laser and low-temperature-grown-GaAs based PC elements, generating observable bandwidth up to 15 THz.[9] Their result was justified by the clearly observed spectral discontinuity due to the phonon resonance of GaAs, between 8 and 9 THz. In parallel, and indeed with faster advancement, all-optical THz systems using optical rectification (OR) and EO sampling have proven to be effective for obtaining ultrabroadband THz waves.[5–7] The broadest observable bandwidth from all-optical THz systems has been reported to be >100 THz, by Kubler *et al.* using an extremely thin GaSe emitter and sensor.[7]

So far, for all the reported THz bandwidths broader than 10 THz, there always exist strong dispersion and absorption gaps associated with the lattice resonance in either the PC materials or crystalline EO materials. If such THz sources and detectors are employed in spectroscopic studies, spectral information in these gaps cannot be extracted. One of the advantages of using amorphous EO polymer films as THz emitters and sensors is that there is no dispersion or absorption resulting from the lattice resonance effect, making a gap-free THz spectrum possible. Another advantage of EO polymer films is the ease of fabrication and handling, in contrast to the extremely thin crystalline EO materials used for existing broadband THz systems.[6,7] In addition, we can engineer the EO polymeric materials to achieve small phase mismatch and high EO coefficients such that brightness and broad bandwidth of THz radiation can be obtained. In this paper, we present an experimental study on a broadband and spectrum-gap-free THz system based on an EO polymer emitter-sensor pair.

The EO polymeric material we worked with is a guest-host mixture of 40% Lemke, a dye molecule, and 60% amorphous polycarbonate (APC), a glassy optically clear polymer. In this paper, we refer to this material as LAPC. The preparation of LAPC has been described elsewhere.[14,15] All the LAPC films were poled normal to the film surface with high electric field (~90 V/μm). After fabrication, we used an ellipsometric technique[16] to measure the EO coefficients of the films. EO coefficients between 25 and 40 pm/V were routinely achieved at 800 nm. We did not observe significant degradation of the performance of these EO polymer films over a few weeks.

By fitting our experimental data to a Sellmeier dispersion formula, the dispersion of LAPC can be expressed as $n_{\mathrm{opt}}^2 = 2.3045 + (0.33636 \times \lambda_{\mathrm{opt}}^2)/(\lambda_{\mathrm{opt}}^2 - 0.512^2)$, where λ_{opt} is the optical wavelength in μm and the peak absorption wavelength is 512 nm. Using the formula, the optical refractive index n_{opt} at 800 nm is calculated to be 1.70, and the optical group index $n_g = n_{\mathrm{opt}} - \lambda_{\mathrm{opt}} \cdot (dn_{\mathrm{opt}}/d\lambda_{\mathrm{opt}})_{\lambda_{\mathrm{opt}}} \approx 1.93$. We estimated the THz refractive index n_{THz} of LAPC to be ~1.8, by doing a THz-TDS measurement (with useful bandwidth of ~2 THz). Since there is no phonon effect in amorphous films, we expect this THz refractive index to be valid even well above 2 THz.

Because a perfect phase match does not exist for LAPC, we expect limited coherence length[8] for the THz emission and detection. The effect of limited coherence length should manifest as spectral dips on the THz spectrum (not the same as absorption gaps). However, these kind of dips have not been pointed out in most papers on ultrabroadband THz emission and detection where the scheme of OR and EO sampling is employed. Leitenstorfer *et al.* predicted a dip of such kind in their modeling, but it occurred in the region near the noise floor of their experimentally obtained spec-

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trum such that it was vaguely identified.[6] To get a clear picture of these phase-mismatch-induced dips, a set of emitters or sensors, from extremely thin to moderately thin, is needed. However, this is impractical when using crystalline EO materials, due to the fabrication difficulty and cost. On the other hand, very thin EO polymer films can be fabricated in a routine process and several films can even be stacked up to be used as a thick emitter or a sensor. Such advantage allows for the flexibility and possibility to picture the phase-mismatch effect in polymeric materials. This study is important since it can be used for guidance to decide on the suitable thickness of polymer emitters and sensors, so as to achieve the best balance between the bandwidth and signal-to-noise ratio (SNR) for experiments.

For this work, we prepared four layers of freestanding LAPC films for emitters, each with a physical thickness of $\sim 70\ \mu$m. Considering the poling geometry and the *p*-polarization of the pump beam in the experiments, we oriented the polymer film such that the pump beam was incident at Brewster's angle in order to achieve the maximal THz emission,[14,15] so each layer had the effective emitter thickness of $\sim 100\ \mu$m. By stacking them up one by one, each oriented with the same poling polarity, we obtained four different thicknesses for emitters: $\sim 100\ \mu$m, $\sim 200\ \mu$m, $\sim 300\ \mu$m, and $\sim 400\ \mu$m. The employment of the multilayer emitters is due to the fact that it is difficult to pole >100-μm thick polymer films with a voltage high enough to obtain good EO coefficients in our lab.

The experimental set-up is the same as what was described elsewhere,[15] except that here we used only reflective optical elements to avoid broadening of the 50-fs (FWHM) pulses (800-nm central wavelength and 1-kHz repetition rate) and only ~ 10 mW (average power) pump beam was focused onto a LAPC emitter, with an elliptical spot of $\sim 6\ \text{mm}^2$, to generate THz pulses. Because of the transverse poling geometry, we rotated the LAPC sensor by an angle of $\sim 45°$ with regard to its poling direction such that there was a projected component of the *p*-polarized THz field along this poling direction, and for the sensitive EO detection, we further rotated the LAPC sensor until the incidence plane was 45° with respect to the probe beam polarization. With this orientation taken into consideration, the thickness of the LAPC sensor was estimated to be $\sim 180\ \mu$m.

Figure 1 shows the amplitude spectra of the THz fields from the four LAPC emitters, using the same 180-μm thick LAPC sensor in each case. Each result was obtained by averaging 10 traces in the time domain and Fourier transforming the averaged THz field to the frequency domain. The time constant of the lock-in was set at 100 ms. For the 100-μm thick LAPC emitter, the observable bandwidth is ~ 12 THz and free of spectral gaps. For the 200-μm thick LAPC emitter, the observable bandwidth is narrowed to ~ 11 THz. It is very interesting to note that, for the 300-μm and 400-μm thick LAPC emitter, there are clear phase-mismatch induced dips. For the former one, the dip is located around 5 THz, and for the latter one, one dip is located at ~ 4 THz and the other at ~ 8 THz.

In order to prove that these dips are due to phase-mismatch, we have developed a model for THz systems based on OR and EO sampling, which includes the effect of group velocity dispersion (GVD) on the broadening of the pump and probe pulses. The predicted spectral dips by our model match the experimental results. We have found that

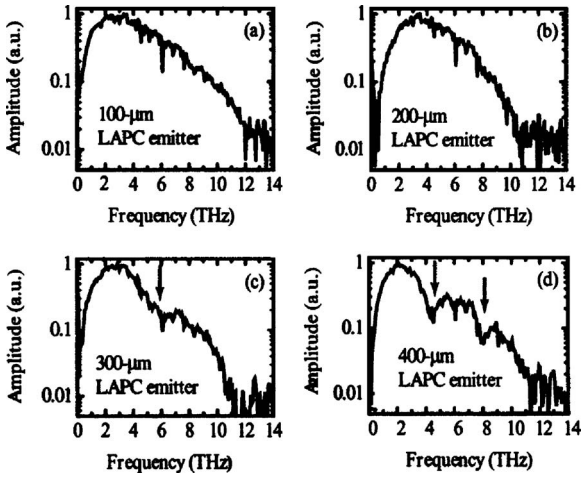

FIG. 1. Fourier-transform amplitude spectra of the THz waves emitted by (a) a 100-μm thick LAPC emitter, (b) a 200-μm thick LAPC emitter, (c) a 300-μm thick LAPC emitter, and (d) a 400-μm thick LAPC emitter, respectively. In all these cases, a 180-μm thick LAPC sensor was used. The arrows indicate the spectral dips resulting from the phase-mismatch in the LAPC emitters.

inclusion of the GVD effect is essential. When the pulse broadening GVD effect is not considered, as in the work by Caumes *et al.*,[17] the amplitude of the THz wave generated via OR in a EO medium is $\propto \sin c[\pi \cdot \Omega \cdot (n_{\text{THz}} - n_g) \cdot z/c] = \sin c[(\pi \cdot z)/(2l_c)]$, where Ω is the THz frequency, z is the thickness of the EO medium, c is the speed of light, and $l_c = c/(2\Omega \cdot |n_g - n_{\text{THz}}|)$ is the coherence length first presented by Nahata *et al.*[8] neglecting the GVD effect of the EO medium. Using their model, a 300-μm LAPC emitter should exhibit a spectral dip at ~ 7.7 THz and 400-μm LAPC emitter should exhibit two spectral dips at ~ 5.8 THz and 11.6 THz, respectively, below 12 THz. Those predictions are not consistent with our experiments. The failure of their model can be explained by the fact that the group index cannot be considered to be a constant in our case where ~ 50-fs-FWHM pulses with a spectral bandwidth of ~ 30 nm and a dispersive material are used. The assumption of a constant group index usually holds true for the case where >100-fs-FWHM pulses with a bandwidth of <10 nm are used, however. The results presented here match quite will with those predicted from a model we have developed that includes the effect of GVD, which we will publish elsewhere.

Since the observable bandwidth in these four cases all occurs between 10 and 12 THz, we conclude that this region is where the spectral dip resulting from the 180-μm thick LAPC sensor is located. The difference in the thickness for the four LAPC emitters can shift this dip location only within a small region. Many water absorption lines are observed for the four spectra, because the air of the experiments was not completely dry. The THz field peak-to-peak amplitudes in these four cases were quite comparable, leading to the conclusion that there is no need to use an LAPC emitter thicker than 200 μm to achieve useful and smooth bandwidth to ~ 12 THz. For much thinner LPAC emitters and sensors, the bandwidth below where the first phase-mismatch induced dip occurs would be broader, but the signal amplitude would be lower and the SNR that could be achieved with reasonable averaging time would not be as high as for thicker emitters such that the full bandwidth may not be observed.

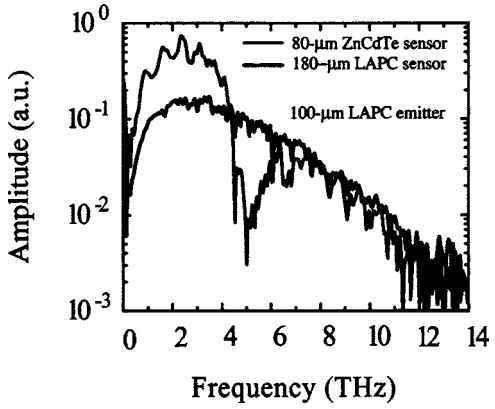

FIG. 2. Fourier-transform amplitude spectra of the THz waves generated by a 100-μm thick LAPC emitter and detected by a 180-μm thick LAPC sensor (solid black line) and an 80-μm thick ZnCdTe sensor (solid gray line), respectively. The spectral gap around ~5 THz is due to the lattice resonance effect in the ZnCdTe crystal.

Because ZnTe and some other EO crystals with similar crystallographic structure have been used as standard THz emitters and sensors, it is meaningful to compare the performance of our LAPC films with one of such EO crystals for the emission efficiency or detection sensitivity. We had a ~80-μm thick ZnCdTe crystal available and used it as the THz sensor to compare with our 180-μm thick LAPC sensor. Figure 2 shows the comparison of the amplitude spectrum between the ZnCdTe sensor and the LAPC sensor, where the same 100-μm thick LAPC emitter was used. For the ZnCdTe sensor (gray line), there is a strong absorption gap around 5 THz, in contrast to the continuous spectrum from the LAPC emitter-sensor pair (black line). This gap-free feature of the polymer emitter-sensor pair is especially promising for THz-TDS applications because richer and more complete spectroscopic information can be obtained. The locations of the water absorption lines above 7 THz are well overlapped for both spectra. The ZnCdTe sensor is about 4 times more sensitive than the LAPC sensor for lower frequencies around 2 THz, which is due to the fact that there is a good phase-match in ZnCdTe in that spectral region. On the other hand, the phase-mismatch in LAPC is constant in the whole observable THz range ($n_g - n_{\mathrm{THz}} \approx 0.13$), and not as good as ZnCdTe around 2 THz, for the 800-nm probe wavelength. The other reason for the lower sensitivity of LAPC sensor is due to the poling geometry. As explained above, only the projected component, not the full strength of the THz field, is measured. This issue can be solved by turning to in-plane poling geometry in the future. It can also be tackled by using optical wavelengths that lead to smaller phase-mismatch, and above all, by designing and synthesizing polymeric materials with very high EO coefficients and/or smaller phase-mismatch. Multiple internal reflections inside the ~80-μm thick ZnCdTe crystal explain the ~0.7-THz-period spectral modulation, and this effect is mostly eliminated in the case of the LAPC sensor due to the oblique incidence of the THz field and the lower refractive index of LAPC.

In summary, we have achieved a gap-free THz spectrum up to ~12 THz from our THz system based on the LAPC emitter-sensor pair. We have also done an experimental study on the effect of phase mismatch on the THz spectrum obtained from our system. Spectral dips due to the phase mismatch have been clearly observed. The results of this study can be used as guidance to determine the thickness of the polymer emitters and sensors needed to achieve balanced SNR and bandwidth in future THz spectroscopic applications. A comparison has been done between the ZnCdTe sensor and the LAPC sensor. It is very promising that EO polymeric materials can be employed for efficient THz emitters and sensors providing broad THz bandwidth, by careful material engineering.

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