Coherent transitions between the shallow acceptor levels in germanium using intense THz pulses

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Abstract. Nonlinear transmission spectroscopy was performed on a doped Ge:Ga semiconductor using intense THz pulses with different cycle numbers. When single-cycle pulses were used, non-perturbative phenomena, such as the ionization of shallow impurities, competed with the conventional coherent transition, whereas the coherent transition was dominant when multi-cycle pulses were used.

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1. Introduction

Coherent transitions in two-level atomic systems, which are generally described by the area theorem, are one of the most fundamental problems in nonlinear optics [1]. The coherent transition in a Rydberg atomic system has been demonstrated using easily controllable single-cycle radio frequency (rf) pulses [2], and is known to depend on the carrier envelope phase of the excitation pulse, where the area theorem is no longer valid. Therefore, coherent transitions using single-cycle rf pulses may allow hidden aspects of light–matter interactions to be explored.

An intense single-cycle THz pulse has been generated using a non-resonant optical rectification process [3]. The phase of the THz pulses is locked and the maximum electric field is greater than 1 MV cm$^{-1}$ [4, 5]. Nonlinear spectroscopy has been demonstrated using these THz pulses in semiconductors for the nonlinear transport and inelastic scattering of free carriers, and excitonic polarization modulation near the semiconductor band gap [6–13]. Hence, these single-cycle phase-locked THz pulses are already sufficiently strong to investigate the coherent transition in two-level systems.

Ga-doped germanium (Ge:Ga) is one of the most widely used doped semiconductors, and its use in far-infrared lasers has been extensively investigated [14]. The binding energy of the acceptor is 11 meV, and its energy diagram has been assigned [15] by analogy with that of a Rydberg atom. This means that Ge:Ga is an ideal material for studying coherent phenomena using THz pulses. In the current study, we performed nonlinear spectroscopy on a Ge:Ga crystal using intense THz pulses produced by the tilted pulse front technique. The nonlinear transmission spectrum depends on the waveform of the THz pulses because of the competition between the coherent transitions obeying the area theorem and the non-perturbative phenomena.

2. Experimental setup

A 0.5 mm thick Ge:Ga single crystal with a dc resistance of 2 $\Omega$ cm, corresponding to a carrier density of $7 \times 10^{15}$ cm$^{-3}$ and a hole mobility of 1900 cm$^2$ V$^{-1}$ s$^{-1}$, was used. Figure 1 shows the spectra of $-\log T$ in the THz frequency region, where $T$ is the transmissivity of the crystal. The spectra were obtained by THz time-domain spectroscopy with a spectral resolution of 0.08 THz. The value of $-\log T$ roughly represented the absorption coefficient of the weak THz pulse incidence. At 300 K, the value of $-\log T$ was high in the low-frequency region, owing to free carrier absorption. We used a simple Drude model to estimate the carrier density as $2 \times 10^{15}$ cm$^{-3}$ from complex transmission coefficients, under the assumption that the effective
mass was $0.37m_0$. This low-frequency component disappeared at 10 K, and two sharp absorption lines appeared at 2.03 and 2.22 THz. The transmission spectrum of another 0.5 mm thick Ge:Ga single crystal with a resistance of 0.2 $\Omega$ cm was also measured; however, free carrier absorption appears even at 10 K. This difference was caused by the metal–insulator transition, because the expected carrier density of the high-resistance crystal was below the Mott density, $n_M = 1/(4/3\pi a_B^3) = 4 \times 10^{15}$ cm$^{-3}$, whereas that of the low-resistance crystal was above the Mott density. The Mott density was calculated using the Bohr radius of the lowest acceptor level, $a_B = 40$ nm. Therefore, the two absorption lines originated from transitions between the shallow acceptor levels. The degenerate wave functions for a given acceptor level were transformed for a $\Gamma_6$, $\Gamma_7$ or $\Gamma_8$ irreducible representation of the double tetrahedral group. The ground state $(8+01)$ had $\Gamma_8$ symmetry and envelope functions with even parity [16]. Thus, the 2.03 and 2.22 THz absorption lines were assigned to the D line (transition to the $(8–02)$ level) and the C line (transition to the $(7–0)$ level), respectively [15]. The energy diagram is shown in the inset of figure 1.

The experimental setup for the nonlinear transmission measurements was similar to that reported elsewhere [17, 18]. Optical pulses from an amplified Ti : sapphire laser system were used (1 kHz, 580 mW, 780 nm, 200 fs). The excitation beam, which had its pulse front tilted by means of a grating and a lens pair, was incident on a Mg-doped (1.5%) LiNbO$_3$ prism THz emitter [19]. The THz pulses were guided by four Au-coated parabolic mirrors into the sample and an electro-optic (EO) detector, which was a 1 mm thick (110)-oriented ZnTe crystal. To measure the field amplitude dependence of the transmission over a wide range with the maximum field above the saturation level of the EO detector, we placed wire grid polarizers before and after the sample, and altered the field amplitude at the sample by rotating the
azimuthal angles of the two polarizers. The field amplitude incident on the EO detector was kept constant; when the field amplitude at the sample was decreased by rotating the first polarizer, the transmission through the second polarizer was increased to compensate for the field reduction. This allowed amplitude-dependent transmission spectra to be obtained with satisfactory signal-to-noise ratios for incident amplitudes of \( E_0 \) (0.2 kV cm\(^{-1}\)) for fields up to 16\( E_0 \). The electric field profile was measured in the time domain by varying the time delay between the probe beam and the THz beam. Two 2 THz bandpass filters were added before the sample to shape the THz pulses. The filter was fabricated from 30 μm thick metal foil with holes arranged in a triangular lattice. The power spectra of the multi-cycle and single-cycle excitation pulses are shown in figures 1(a) and (b), respectively. The spectrum of the multi-cycle pulse covered the D line resonance at 2.0 THz, and had a sharp peak at 2.2 THz arising from the surface mode of the filter, where the polarization was rotated. Therefore, another polarizer was placed in front of the second polarizer pair. For the single-cycle pulse, the spectral components above 2.8 THz (12 meV) were small because of the strong absorption of the emitter, and the direct photoionization of the shallow acceptor levels was negligible [20].

3. Experiments

Figure 2 shows the temporal profile of the incident THz pulses (thin curves) and the reemission (thick curves) from Ge:Ga. The field amplitudes of the incident THz pulses were calibrated in the crystal by multiplying the Fresnel coefficient, \( 2/(n_{Ge} + 1) \), by the refractive index of the crystal \( n_{Ge} \). The reemission indicated the free induction decay of the polarization induced by the incident field. The destructive interference between the incident and the reemitted fields attenuated the transmitted electric field. The reemission component was calculated from the difference between the incident and transmitted electric fields, where the transmitted field was compensated for in the crystal by dividing the Fresnel coefficient, \( 2n_{Ge}/(n_{Ge} + 1) \). For the multi-cycle pulse excitation (figure 2(a)), the reemission continued for longer than the incident pulse duration. The reemission was gradually suppressed as the amplitude of the incident pulse increased. The reemission disappeared at the end of the incident pulse for an incident pulse field of 8\( E_0 \) (maximum electric field of 1.6 kV cm\(^{-1}\)). This was characteristic of the saturated absorption of the D line. Similar behaviors in the time domain have been reported using intense phase-locked multi-cycle resonant pulses [21, 22]. However, at a field amplitude of 16\( E_0 \) (maximum electric field of 3.3 kV cm\(^{-1}\)), the reemission reappeared with a different phase and period, which may have been influenced by the reemission of the C line.

The reemission was also examined in the frequency domain. The power spectra of the reemission normalized by the incident field are shown in figure 3(a). The reemission at 2.04 THz was reduced as the field amplitude increased, and it completely disappeared for the incident pulse with an amplitude of 16\( E_0 \). However, the reemission at 2.20 THz remained. This change in the reemission was probably caused by Rabi flopping [21, 22]. Hence, the Rabi frequency was estimated from the field amplitude. The transition between the impurity levels is analogous to that from the 1s ground state to the excited 2p\(_x\) state in a hydrogen atom, and can be expressed as \( \omega_R = \mu E_0/\hbar = 2^{15/2} e E a_B /3^5\hbar \), where \( \mu \) is the transition dipole moment, \( \hbar \) is the reduced Planck constant, \( e \) is the elementary charge and \( E \) is the field amplitude [1]. However, it was necessary to compensate for the oscillator strength of the D line (\( f = 0.095 \)) [23] being smaller than that of the 1s–2p transition in an ideal hydrogen atom (\( f = 0.42 \)). Thus the transition dipole moment was evaluated as \( \mu = 67 e \) Å, and the period of the Rabi oscillation was \( 2\pi/\omega_R = 2.1 \) ps.
for $E = 3\, \text{kV cm}^{-1}$. This was comparable with the pulse duration of the multi-cycle pulses, which suggests Rabi flopping was possible.

For the single-cycle THz pulse excitation (figure 2(b)), the electric field oscillation at 2.04 THz also appeared after a delay. Its amplitude decreased as the incident field amplitude and the low-frequency component increased at the beginning. For the incident field amplitude of $16E_0$ (maximum field amplitude of 6.4 kV cm$^{-1}$), the slow component was dominant. This behavior was clearer in the frequency domain. The reemission at 2.04 THz decreased with the amplitude of the incident pulse and the reemission component below 0.5 THz increased (figure 3(b)).

4. Numerical simulation and discussion

The Rabi flopping of the electric transition using high-field few-cycle infrared pulses has been investigated experimentally [21, 22, 24], and has been analyzed using density matrix...
Figure 3. Reemission spectra from Ge:Ga normalized by the amplitude of the incident THz pulse, excited with (a) multi-cycle pulses and (b) single-cycle pulses.

equations. Casperson discussed the validity of the conventional density matrix equations for the few-cycle pulse excitation [25]. We calculated the temporal evolution of the polarization to explain the responses for the single-cycle and multi-cycle pulse excitation. We assumed two electronic transitions: the transition from the lowest level, level 1, to an excited level, level 2, with an energy difference of $h\nu_{12}$ (D line); and the transition from level 1 to an excited level, level 3, with an energy difference of $h\nu_{13}$ (C line). Neglecting the permanent dipole moments ($\mu_{11} = \mu_{22} = \mu_{33} = 0$), the density matrix equations with the incident electric pulse $E(t)$ are expressed as

$$\frac{d\rho_{33}}{dt} = -\gamma_{1,13}\rho_{33} - \frac{i}{\hbar} E(t)(\mu_{13}\rho_{31} - \mu_{13}^*\rho_{31}^*),$$

$$\frac{d\rho_{22}}{dt} = -\gamma_{1,12}\rho_{22} - \frac{i}{\hbar} E(t)(\mu_{12}\rho_{21} - \mu_{12}^*\rho_{21}^*),$$

$$\frac{d\rho_{11}}{dt} = \gamma_{1,12}\rho_{22} + \gamma_{1,13}\rho_{33} + \frac{i}{\hbar} E(t)(\mu_{12}\rho_{21} - \mu_{12}^*\rho_{21}^*) + \frac{i}{\hbar} E(t)(\mu_{13}\rho_{31} - \mu_{13}^*\rho_{31}^*),$$

$$\frac{d\rho_{21}}{dt} = -\frac{d\rho_{12}^*}{dt} = -(i2\pi\nu_{12} + \gamma_{2,12})\rho_{21} - \frac{i}{\hbar} E(t)\mu_{12}(\rho_{22} - \rho_{11}),$$

$$\frac{d\rho_{31}}{dt} = -\frac{d\rho_{13}^*}{dt} = -(i2\pi\nu_{13} + \gamma_{2,13})\rho_{31} - \frac{i}{\hbar} E(t)\mu_{13}(\rho_{33} - \rho_{11}),$$

where $\rho$ is a density matrix element, and $\gamma_1$ and $\gamma_2$ are the longitudinal and transverse relaxation constants, respectively. The initial values of the density matrix elements were $\rho_{11} = 1$, $\rho_{22} = \rho_{33} = 0$ and $\rho_{12} = \rho_{13} = 0$. The parameters for the transition were $\mu_{12} = 67e\text{Å}$, $\nu_{12} = 2.03\text{THz}$ and $\nu_{12} = 2.22\text{THz}$. We used $\mu_{13} = 37e\text{Å}$, which was calculated from an oscillator strength of $f = 0.053$ for the C line [23]. In our simulation, $\gamma_1/2\pi = 0\text{THz}$ and $\gamma_2/2\pi = 0.05\text{THz}$. 

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The intrinsic widths of the D and C lines are narrow for low Ga concentrations; however, the concentration of Ga was close to the Mott density in our sample, which caused spectral broadening arising from the many-body effect. Thus, we calculated the temporal evolution of the density matrix elements using these parameters. Although the diagonal elements represent the population of electrons in each level, the off-diagonal elements are closely related to the polarization, $p$, by the number of electrons in the system, $N$,

$$p = N \left( \mu_{12} \rho_{21} + \mu_{21}^* \rho_{12}^* + \mu_{13} \rho_{31} + \mu_{31}^* \rho_{13}^* \right).$$

The sample thickness of 0.5 mm reminds us of the need to consider the propagation effect. Generally, nonlinear pulse propagation in a coherent system has been treated as self-induced transparency, in which a pulse with an area larger than $\pi$ splits into multiple ones [26]. However, the present result does not appear to reflect such an effect. Thus, we neglected the propagation effect and treated the first-order derivative of $p$ in our simulation as the reemission [21].

Figure 4 shows the reemission profiles as functions of time at different incident field amplitudes. The topmost profiles are those of the incident single-cycle and multi-cycle pulses that we used to model the incident pulses shown in figure 2. The experimental results in figure 2(a) were almost reproduced by the calculations; the amplitude of the reemission normalized by the incident field amplitude was gradually suppressed when the incident pulse intensity was increased. Furthermore, another reemission appeared at an amplitude of $16E_0$, which was in phase with the incident pulse. This indicates that complete Rabi flopping occurred for the multi-cycle pulses. Figure 4(b) also shows that resonant reemission was gradually suppressed and another in-phase reemission appeared, even for the single-cycle excitation at $16E_0$. This contradicts the experimental results. The corresponding spectra for the simulated reemission are shown in figure 5. The spectral shape in figure 5(a) is very similar to that in figure 3(a), except for the intensity of the C line, which is lower than that in figure 3, because we assumed no other transitions in our simulations. However, there are clear differences between the experimental (figure 3(b)) and the simulation (figure 5(b)) results for the single-cycle excitation. From this we conclude that the simple area theorem cannot explain the single-cycle excitation of the three-level system.

The temporal evolution of the excited level 2 population is shown in figure 6. For the multi-cycle excitation (figure 6(a)), $\rho_{22}$ approached 0.8, whereas $\rho_{33}$ approached 0.2. This can be approximated as Rabi flopping between level 1 and level 2 at an incident amplitude of $\sim 10E_0$. However, for the single-cycle excitation, the value of $\rho_{22}$ increased to 0.33 and converged to 0.12.

The difference can be explained by a different nonlinear effect, caused by the ionization of deep impurity centers. This effect has been investigated in Ge using transient tunneling spectroscopy on a nanosecond timescale [27, 28] and using quasi-continuous-wave submillimeter beams [29]. Multiphonon-assisted tunneling ionization is dominant at relatively low incident electric-field amplitudes, where the impurities are ionized through the Poole–Frenkel effect. In contrast, the impurity centers can be directly ionized through tunneling at very high incident electric-field amplitudes without thermal activation, even at low temperatures. The theory of the direct tunneling process has been expanded from the dc field effect model, and its characteristic field amplitude, Blossy’s critical dc field, is $8.9 \text{kV cm}^{-1}$ [30]. Because the maximum incident field of $6.4 \text{kV cm}^{-1}$ for $16E_0$ (figure 2(b)) was similar to the critical value, the level diagram was strongly modulated by the incident field. We did not measure temperature dependence; therefore, our experiments did not reveal the
Figure 4. Simulated profiles of the reemission normalized by the amplitude of the incident pulses. The maximum incident field amplitudes for $16E_0$ were (a) $3\, \text{kV cm}^{-1}$ and (b) $6\, \text{kV cm}^{-1}$. The topmost profiles are those of the incident pulses.

Figure 5. Simulated spectra of the reemission normalized by the amplitude of the incident pulses, excited with (a) multi-cycle pulses and (b) single-cycle pulses.

details of the ionization process. However, the slowly oscillating component at an amplitude of $16E_0$ (figure 2(a)) can be assigned as the emission from the real current of the ionized carriers. In this case, the potential of the shallow acceptors was screened by the ionized carriers, which suppressed the efficiency of coherent transitions further. Therefore, using the
Figure 6.(a) Simulated profiles of the diagonal elements, $\rho_{22}$ (solid curves) and $\rho_{33}$ (dotted curves), at different incident field amplitudes for multi-cycle excitations. The topmost profiles are the incident pulses. (b) Simulated profiles of the diagonal elements, $\rho_{22}$, at the maximum incident field amplitude for single-cycle excitations with a different phase.

single-cycle pulse, the ionization of the shallow acceptors occurred before the Rabi flopping. The competition between coherent transitions and ionization was visible even with multi-cycle THz pulse excitation [22].

We observed another interesting phenomenon, which was different from the dc field effects. Figure 6(b) also shows the temporal evolution of the population, $\rho_{22}$, thin curve for single-cycle pulses with a different carrier envelope phase. Although the power spectrum was the same, the temporal evolution of $\rho_{22}$ was very different. The final value of $\rho_{22}$ was strongly suppressed ($\rho_{22} = 0.06$), which implies that the coherent transition was strongly influenced by the phase of the THz pulses. This phase dependence has been demonstrated for atomic excitation with rf pulses [2, 31–33]. We have recently achieved the phase control of single-cycle THz pulses using artificial dispersive optics [34]; therefore, we can now experimentally investigate the phase dependence of coherent transitions in the THz frequency region.

5. Conclusions

We performed nonlinear transmission spectroscopy for a Ge:Ga crystal using intense single- and multi-cycle THz pulses. Although a coherent two-level transition between the shallow acceptor levels was dominant for the multi-cycle THz pulses, for the single-cycle pulses different nonlinear phenomena, such as the ionization of the shallow acceptors, became dominant in the dc field and competed with the coherent transition. These results strongly suggest that the number of cycles of the excitation pulse influences nonlinear behavior, even in the same material.

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