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Ultrafast Two-Dimensional Time-Domain Spectroscopy of Hydrogen-Like Impurity Centers in Germanium

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***Abstract*—Coherence lifetimes (T_2) of excited states of a hydrogen-like arsenic donor in germanium (Ge:As) have been determined by nonlinear two-dimensional (2D) ultrafast time-domain terahertz spectroscopy at cryogenic temperatures. The derived coherence times for the $2p_0$ and $2p_\pm$ donor states are 2 ps and 0.15 ps respectively.**

I. Introduction

TWO-DIMENSIONAL Terahertz time-domain spectroscopy has shown to be an effective tool for analysing nonlinear processes such as resolving multi-level dynamics in quantum well systems [1], including intersubband saturable absorbers [2] and QCLs [3]; graphene [1]; and vibrational spectroscopy of semiconductor phonons [4].

Impurity centers in semiconductors have long been studied [5] but in recent years have gained attention for applications as sources and detectors in the THz range [6-7] as well as for coherent control of spin orbitals for quantum computing [8] owing to their long-lived states. For these applications, 2D time-domain spectroscopy presents some benefits over single-frequency photon-echo techniques [8] since it should be possible to determine the transition relaxation times of several transitions simultaneously and monitor multi-level relaxation pathways over ultrafast time scales.

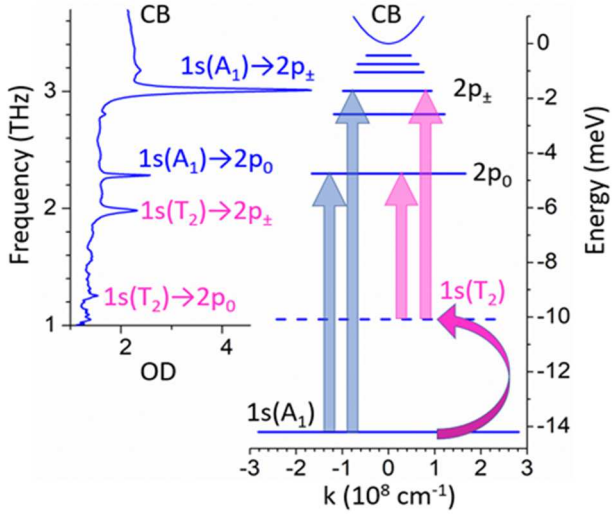

Fig. 1. Energy level diagram of Ge:As, highlighting the main absorbing transitions from the $1s(A_1)$ and $1s(T_2)$ states. Energy level values taken from [5].

II. Sample and Setup

The sample under investigation is a 3 mm thick, wedged germanium crystal with a $9x10^{14}$ cm^{-3} Arsenic doping concentration (Ge:As), cooled to <10 K using a liquid He flow cryostat. The representative energy spectrum of the As donor is shown in Fig. 1. The transitions from the ground state, $1s(A_1)$, into the excited $2p_0$ and $2p_\pm$ states have the largest oscillator strengths and are within the spectrum of the THz sources used for this experiment. Owing to imperfect thermal coupling to the cold finger, there is also a non-vanishing population of the $1s(T_2)$ state, therefore, two additional transitions occur in absorption spectra to the $2p_0$ and $2p_\pm$ states.

A photoconductive array [9] and a BNA crystal [10] were used to producing peak fields of 60 $kVcm^{-1}$, labelled ε_A and ε_B respectively. An amplified laser system generating 40 fs pulses at a center wavelength of 800 nm at a repetition rate of 1 kHz was used to excite both emitters. The pulses were combined using a silicon beamsplitter before being focused onto the sample using a parabolic mirror (see Fig. 2). The pump pulses are chopped 90° out of phase to allow

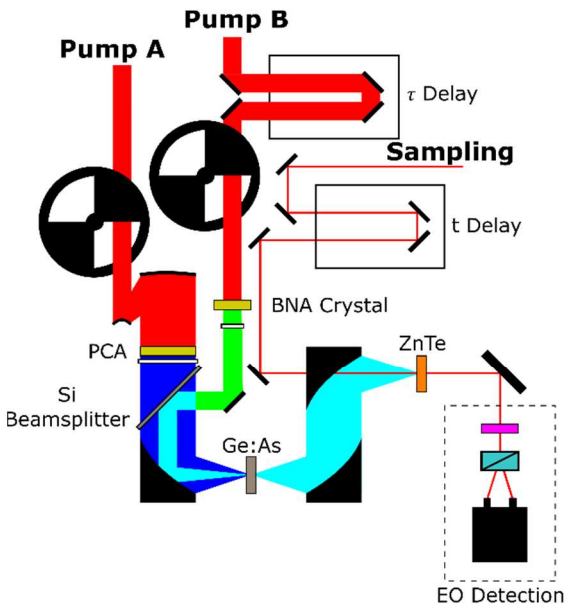

Fig. 2. System diagram of the experimental system used to perform the measurement. A PCA and a BNA crystal are used to produce the two excitation pulses and are combined using a Si beamsplitter before being focused onto the Ge:As sample using an off-axis parabolic mirror. Expanded PTFE filters are placed after the emitters to block the excess IR excitation beam.

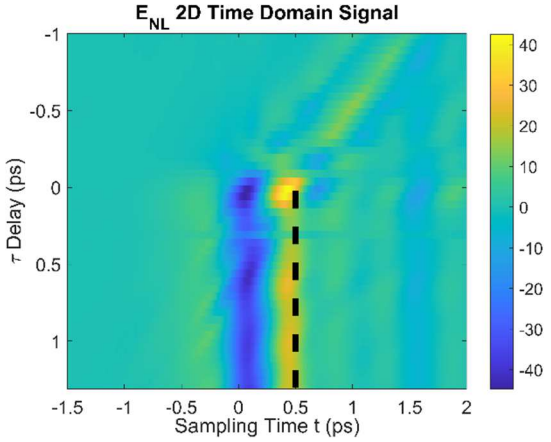

Fig. 3. The 2D nonlinear signal obtained from the measurement of the Ge:As sample. The dotted line highlights the slice used for fitting in Fig. 5.

the four pulse combinations: ε_{AB}, ε_A, ε_B and ε_0 to be acquired for each scan. The delay between ε_B and ε_A (τ) alongside the delay of the sampling pulse (t) are altered throughout the measurement to acquire a two-dimensional signal. The electric field of the THz pulses were detected by electro-optic sampling, using a 1 mm thick ZnTe crystal, providing a detectable bandwidth of 3 THz.

III. Results

The nonlinear response of the sample is calculate using the formula $\varepsilon_{NL} = \varepsilon_{AB} - \varepsilon_A - \varepsilon_B$ and is shown in Fig. 3, with Fig 4. showing an example of how ε_{NL} is acquired from the four signal states at a single τ delay (horizontal slice of Fig. 3). The oscillation of the polarization appears in the t axis, whilst the coherent system memory appears as an oscillating signal in the τ axis, thus allowing for the population and coherence lifetimes of the states (T_1 and T_2) to be acquired by fitting a slice of the nonlinear signal in the τ axis (dashed line in Fig. 3) [2]:

$$\varepsilon_{NL}(\tau) = \sum_n A_{1,n} \exp\left(\frac{-\tau}{T_{1,n}}\right) + A_{2,n} \sin(\omega_n \tau) \exp\left(\frac{-\tau}{T_{2,n}}\right)$$

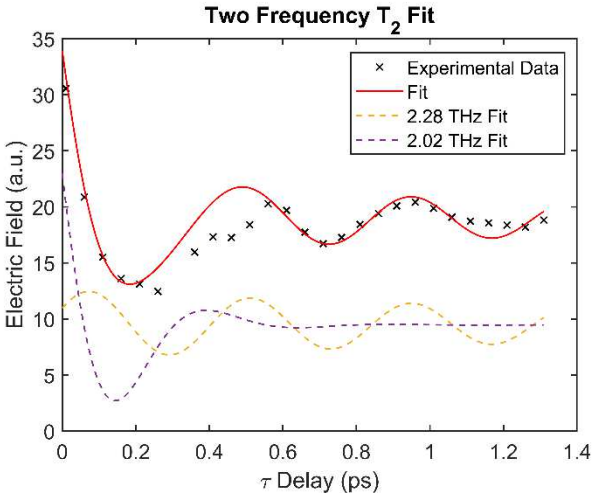

Fig. 5. Slice of the two-dimensional nonlinear signal at $t = 0.5$ ps shown to be the combination of two exponentially decaying sine waves of frequency 2.28 and 2.02 THz, relating to the $1s(A_1)$-$2p_0$ and $1s(T_2)$-$2p_\pm$ transitions. The T_2 values of the transitions are 2 and 0.15 ps for the 2.28 THz and 2.02 THz transitions respectively.

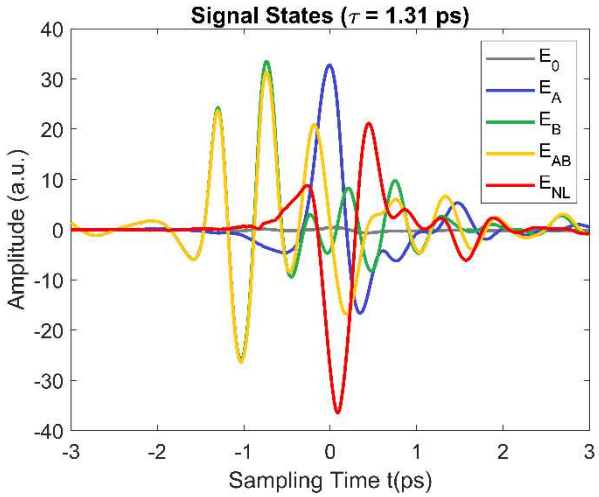

Fig. 4. Four signal states acquired from a measurement at a single τ delay (1.31 ps). ε_A is generated using a PCA [9] whilst ε_B is generated using a BNA crystal [10]. The peak field of both pulses on the sample was measured as 60 kVcm^{-1}. The nonlinear signal shown in red is obtained by performing $\varepsilon_{AB} - \varepsilon_A - \varepsilon_B$.

where, the index, n, denotes the transition(s) involved. The T_1 decay times of the $2p_0$ and $2p_\pm$ donor states were derived in pump-probe experiments as 0.8 ns and 0.6 ns, correspondingly [11], much larger than the timescale of this measurement, meaning that $A_1 \exp(-\tau/T_1) \approx A_1$. Attempting to fit for T_2, it was found that the expected exponentially decaying sine wave of 2.28 THz ($1s(A_1)$-$2p_0$) was observed ($T_2 = 2 \pm 1$ ps), alongside another lower frequency decaying sine wave of 2.02 THz ($T_2 = 0.15 \pm 0.04$ ps), likely from the $1s(T_2)$-$2p_\pm$ transition. The resulting fit is shown in Fig. 5. Further results, including THz excitation field dependence will be presented.

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