Coherent Anti-Stokes Raman Scattering Spectroscopy in Terahertz Region Using Chirped Optical Pulses

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***Abstract*— We report a novel technique for detection of coherent anti-Stokes Raman scattering (CARS) signal in terahertz (THz) frequency region (THz-CARS). Two frequency-chirped broadband optical pulses are used as the pump and the CARS signal is detected in time-domain after the pulse compression. The results measured for several samples, such as GaSe, are presented and discussed.**

I. Introduction

Terahertz (THz) time-domain spectroscopy is now widely used for low-frequency (< 100 cm^{-1}) absorption spectroscopy and is successful in detecting low-frequency vibrational modes, such as inter-molecular vibrations in organic crystals. On the other hand, low-frequency Raman spectroscopy is not cultivated as much as done for the low-frequency absorption spectroscopy, mostly because of the relative difficulty to detect low-frequency Raman spectra compared to other frequency regions. Strong Rayleigh scatterings sometimes overwhelm the signals for powdered samples or samples with rugged surfaces. Fluorescence can be another problem for biological samples. In this paper we report a novel technique for detection of coherent anti-Stokes Raman scattering (CARS) signal in terahertz (THz) frequency region (THz-CARS).

Since a femtosecond (fs) pulse has a broad spectral bandwidth, from several THz to a few tens of THz depending on the pulse width, a part of its spectrum can be used as the pump and other part can be used as the Stokes light to excite coherent vibrations with THz frequencies in materials. However, a simple spectral division of the fs laser by filters or other dispersive optics will result in low excitation intensity since other part of the spectrum which is not used for excitation is discarded. To avoid this problem and utilize the broadband spectrum of a fs laser efficiently, chirped fs laser pulses are used as the pump and Stokes pulse in our method. The CARS signal generated in this way is also frequency-chirped, which can be detected after its pulse-compression by using appropriate dispersion compensation optics and separated from the pump pulses in time-domain. The results measured for several samples, such as GaSe, are presented and discussed.

II. Experimental

Femtosecond (fs) laser pulses from a regenerative amplifier of Ti: sapphire laser (Hurricane system from Spectra Physics, $\delta t \sim 120$ fs, $\lambda \sim 800$ nm, 1 kHz, 800 μJ/pulse) were firstly split into the pump and probe pulses. The pump pulses were positively chirped with a grating-lens pair and stretched to about 30 ps. The stretched pump pulses were further split into two beams and recombined with a Michelson interferometer. When the two chirped pulses were superimposed with a slight time delay $\Delta\tau$, the instantaneous frequencies of the two pulses (one is the pump, ω_p, and another is Stokes, ω_S) were shifted by $\delta\omega$ depending on the chirp rate. Thus, they generated an optical beat with a beat frequency $\delta\omega$. This optical beat created an oscillatory polarization with frequency $\delta\omega$ in the sample, which scattered pump light with an up-shifted frequency by $\delta\omega$, resulting in the coherent anti-Stokes Raman scattering with a frequency $\omega_{AS}=2\omega_p-\omega_S=\omega_p+\delta\omega$. Since the carrier frequency of the pump and Stokes pulses was chirped, the CARS signal was also chirped with the same chirping rate (See Fig. 1(a)).

Since the frequency shift of THz-CARS signal was small, it was spectrally overlapped with the strong pump and Stokes spectra. In addition, the CARS signal beam was almost collinear with the pump or Stokes beam due to the phase-matching condition $\mathbf{k}_{AS}=2\mathbf{k}_p-\mathbf{k}_s\cong\mathbf{k}_p(\cong\mathbf{k}_s)$. Therefore, separation of the CARS signal from the pump and Stokes beam is difficult with the usual frequency selective or spatially resolving technique. To overcome this problem, we compressed these chirped pulses by using a compressor grating pair. After compression, the pump and Stokes pulses returned to the original fs pulses with a time interval of $\Delta\tau$. The CARS signal was also converted to a fs pulse, which was advanced in time by $\Delta\tau$ from the pump pulse because of the frequency up-shift by $\delta\omega$ (See Fig. 1(b)). The CARS pulse was up-converted to ~400-nm light by the sum frequency generation (SFG) with the probe pulse in a BBO crystal. The time-resolved (up-converted) CARS signal was finally detected with a GaP photodiode (PD) after passing through a high-pass filter. To increase the signal-to-noise ratio, we modulated the probe beam with an optical chopper at 500 Hz and the signal from the PD was lock-in detected.

III. Results and Discussion

Figure 2 shows the time-domain signal from a (100)-cut ZnSe crystal (thickness = 1 mm), where the time-delay for the probe pulse, τ_1, was scanned for a fixed time difference $\Delta\tau\sim3.2$ ps between the pump and Stokes. Since the chirp rate in our stretcher system was $\delta\omega/\Delta\tau=0.09$ THz/ps, this corresponds to a difference frequency of 0.58 THz. The average power of the pump and Stokes beam incident on the sample was ~0.5 mW, respectively. The coherent anti-Stokes Raman scattering signal is observed at a time delay of 9 ps, which is earlier than the pump pulse by ~3.2 ps, as expected from $\Delta\tau\sim3.2$ ps. The coherent Stokes Raman scattering is also detected after the Stokes pulse. Since there is no optical phonon mode below 5

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THz for ZnSe, the observed signals are attributed to the non-resonant CARS or, in other words, the four-wave mixing process mediated with the two-photon absorption in the conduction bands of this semiconductor.

The CARS spectrum measured for a GaSe crystal (a c-cut, 1-mm thick) is shown in Fig. 3. This spectrum was obtained by the "peak scan", where the time-delay for the probe was changed so that the CARS signal peak shift with the change of the difference frequency $\delta\omega$ was traced ($\tau_1=2\Delta\tau$). The spectrum shows a dispersion-type spectral structure around 0.62 THz (=20.7 cm^{-1}). This structure is explained by the interference between the non-resonant (real and constant in frequency) and the resonant nonlinear optical susceptibility originating from the GaSe E_{2g}-mode (a low-frequency Raman-active mode) [1].

The CARS signal intensity is proportional to the square of the third order susceptibility, $\chi^{(3)}$, which is the sum of the frequency dependent resonant term, $\chi_R^{(3)}$, and the frequency independent non-resonant term, $\chi_N^{(3)}$, each of which is expressed as follows, respectively:

$$\chi_R^{(3)} = \frac{a(\omega_d - \omega_R + i\Gamma)}{(\omega_d - \omega_R)^2 + \Gamma^2} \quad (1)$$

$$\chi_N^{(3)} = \text{constant and real} \quad (2)$$

Here, ω_d ($= \omega_p - \omega_S > 0$) is the difference frequency of the pump and the Stokes frequencies, ω_R is the resonance frequency, and Γ is the half-width of the Raman mode. When the non-resonant contribution is large compared to the resonant one, as is in the present case, the CARS signal intensity is approximated by the following equation [2]:

$$|\chi^{(3)}|^2 = |\chi_R^{(3)} + \chi_N^{(3)}|^2 \cong |\chi_N^{(3)}|^2 + 2\chi_N^{(3)} \frac{a(\omega_d - \omega_R)}{(\omega_d - \omega_R)^2 + \Gamma^2} \quad (3)$$

From the theorical curve fitting to the experimental result shown in Fig. 3, we evaluated the Raman half-width of the GaSe E_{2g}-mode Γ to be 0.2 THz and the ratio of the resonant to the non-resonant contribution, $a/\Gamma/\chi_N^{(3)}$, in the CARS signal to be 0.12.

IV. CONCLUSION

We have suggested and demonstrated a technique for detection of coherent anti-Stokes Raman scattering (CARS) signal in terahertz (THz) frequency region by using frequency-chirped broadband optical pulses as the pump. The CARS signal was separated in time-domain from the pump pulses by the pulse compression and detected by the up-conversion. The results measured for several semiconductor samples, such as ZnSe and GaSe were presented. For the case of GaSe, the resonat CARS spectrum originating from E_{2g}-mode was confirmed. We evaluated the mode line width and the resonant and non-resonant contribution by a theoretical curve fitting successfully. These results indicate the usefulness of this technique for observation of CARS spectra in the THz frequency region.

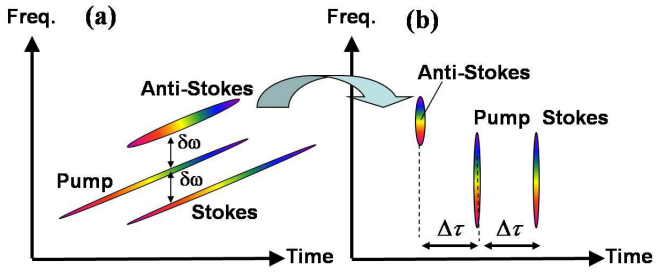

Figure 1. (a) The CARS signal generation and (b) its time -domain separation illustrated in the time-frequency plane.

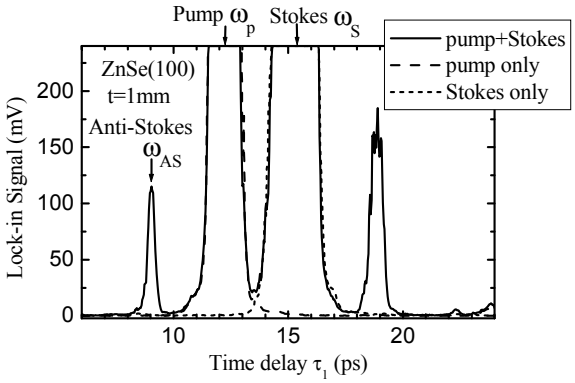

Figure 2. The time-domain signal of the (100)-cut ZnSe crystal (thickness = 1 mm).

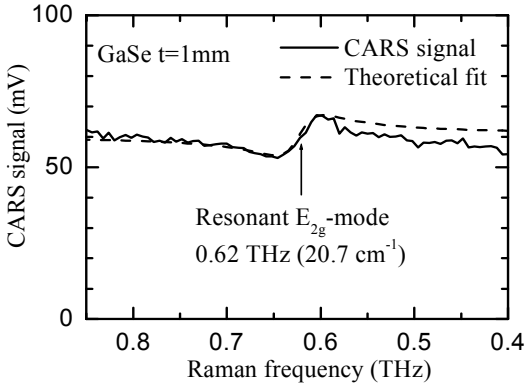

Figure 3. The CARS spectrum of the c-cut GaSe (thickness = 1mm) obtained with the time-domain measurement (the peak scan).

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