Spectral narrowing of four-wave mixing signals for excitons in the layered semiconductor GaSe

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Abstract. The spectral narrowing has been observed using time-resolved and spectrally resolved four-wave mixing measurements on a layered semiconductor GaSe. The narrowing of four-wave mixing spectra is one of the evidences of the non-Markovian dephasing. From the calculation of the non-Markovian theory for exciton-phonon interaction, it has been found that the excitons in GaSe are confined to 7 layers and that the correlation time of the interaction is 1.1 ps, which defines the limit of the non-Markovian time regime.

1. Introduction
Electronic dynamics can be observed as coherent transient phenomena by employing femtosecond pump-probe spectroscopy. By measuring this transient phenomenon, electronic properties are revealed in terms of time domain. Four-wave mixing (FWM) measurement is the method for measuring this dephasing process by using two incident pulses. Exciton polarization induced in a semiconductor by a coherent light pulse is lost by several interactions. Dephasing of exciton polarization is expressed as exponential decay for Markovian dynamics, which is basically treated by the optical Bloch equations. In contrast, exciton polarization of some semiconductors exhibits complicated decay in the initial dephasing. This complicated dynamics are characterized by non-Markovian dynamics of several interactions such as exciton-phonon and exciton-exciton interactions. Beating signals generated by the exciton-phonon interaction have been observed in some semiconductors [1-3]. For exciton-exciton interaction, memory time induced by two pair correlations has been estimated [4]. Because non-Markovian dephasing is determined by the time correlation of interactions, investigations of non-Markovian dephasing are necessary to understand the microscopic behavior of electron dynamics.

As non-Markovian feature, the exciton wave-packet motion has been observed in the layered semiconductor GaSe. It has been found that the wave-packet motion is caused by the exciton-phonon interaction along the c-axis direction, as reported in our previous study [5]. In order to understand the non-Markovian dephasing process, changes of the shape of exciton spectra should be measured in detail. In this study, we report the spectral narrowing of non-Markovian dephasing signals for excitons in the layered semiconductor GaSe. The spectral narrowing was observed using time-resolved (TR) and spectrally resolved (SR) FWM spectroscopy.
2. Experimental details
The sample was a layered semiconductor GaSe, and it was set at 3.4 K in a closed cycle refrigerator. Excitons in GaSe are confined to about 10 layers due to a stacking disorder [6, 7]. Because of the confinement, the dephasing of exciton polarization is caused by the acoustic deformation potential coupling [5]. The excitation source was a frequency-doubled optical parametric oscillator pumped by a mode-locked Ti:sapphire laser tuned to the exciton resonant energy of 2.109 eV. The optical pulse had a duration of 200 fs and a repetition rate of 76 MHz. The first and second excitation pulses were sent into the sample with wave vectors $k_1$ and $k_2$, respectively. The diffracted signal in the direction of $2k_2 - k_1$ was measured at various delay times $\tau$, which is the time interval between the first and second excitation pulses. The TR-FWM signals were detected by using the heterodyne technique with acousto-optic modulators, which were used to shift the frequency of the reference pulse and that of the second excitation pulse. In this technique, the interference of the reference pulse and the FWM signals was detected by a photo detector to which a spectrum analyzer was connected. For the SR-FWM measurements, the signals were spectrally resolved by a monochromator and detected by a photomultiplier tube.

3. Results
The TR-FWM signals are shown in Fig. 1 for various delay times $\tau$. Fast damping is observed only in the initial dephasing at the delay times of 0.0 and 0.4 ps. After the delay time of 0.4 ps, the fast damping gradually disappears and then only the Gaussian signal is observed. The Gaussian signal is created by the distribution of the exciton resonances, i.e., so-called inhomogeneous broadening. However, the fast damping cannot be explained by the phenomenological introduction of inhomogeneous broadening. In order to show the spectral linewidth, the inverse of half-decay time $1/\tau_{1/2}$ is plotted in the inset of Fig. 1, where $\tau_{1/2}$ is measured from the corresponding signal peak. In the inset, $1/\tau_{1/2}$ decreases from 2.9 to 1.5 ps$^{-1}$ with increasing the delay times from 0.0 to 1.0 ps, respectively. This decrease of $1/\tau_{1/2}$ expresses the spectral narrowing.

![Figure 1. Time-resolved four-wave mixing signals for delay times $\tau$. The delay time varies from 0.0 to 2.0 ps in 0.4 ps steps, as indicated. The inverse of half-decay time $1/\tau_{1/2}$ is plotted as a function of the delay time in the inset.](image)

The Fourier transformation of the TR-FWM signal is performed for each delay time as shown in Fig. 2 (a). It is clearly observed that the FWM spectra become narrower with increasing the delay time. The FWM spectrum for the delay time of 0.0 ps extends up to ±5 meV from the center of the spectrum as indicated by the arrows. However, for the delay time of 2.0 ps, the spectrum extends only up to ±2 meV. The spectral narrowing is also observed in SR-FWM measurements as shown in Fig. 2 (b), which is consistent with the Fourier transformation of the TR-FWM signal in terms of spectral narrowing. The asymmetric shape of the SR-FWM signal is caused by the wave-packet motion of exciton coupled to acoustic phonons [5]. It is not
obtained from the Fourier transformation of the TR-FWM signals, because the time evolution of the phase factor cannot be determined from the TR-FWM measurements.

4. Discussion

In order to understand the spectral narrowing of the FWM signals, the dephasing process is discussed on the basis of a microscopic treatment of acoustic phonons, instead of the phenomenological introduction of exponential decay term. In this theoretical treatment, which is characterized as non-Markovian theory [8, 9], exciton polarization is lost by the interaction between excitons and the reservoir of acoustic phonons. The non-Markovian dephasing exhibits only within the correlation time of exciton-phonon interactions. In this time regime, the FWM spectrum is observed as the exciton spectrum involving the spectral broadening due to the correlation. After the loss of the correlation, the linewidth of the FWM spectrum is decreased to the linewidth determined by inhomogeneous broadening. The interaction without the correlation also causes spectral linewidth related to the dephasing, but it is narrower than that of inhomogeneous broadening. The narrowing of the FWM spectra expresses the loss of the correlation.

The full width at quarter maximum (FWQM) of the FWM spectrum is measured for comparing the experimental data with the non-Markovian theory. The FWQM of the SR-FWM signals and the fitting result are shown in Fig. 3. In the fitting, the spectral density of the interaction, which has been analyzed from the wave-packet motion observed in GaSe [5], is applied to the non-Markovian theory. The localization length of excitons is found to be 7 layers, which is consistent with the previous investigations [5-7]. In addition, the correlation time of the interaction is obtained as 1.1 ps, which defines the switching time from the non-Markovian to Markovian dynamics. Because the interaction behaves as inhomogeneous broadening only for the non-Markovian dynamics [8], this result indicates that the dephasing can be suppressed if the second excitation pulse arrives within a few picoseconds. In fact, the decoherence suppression of the excitons in GaSe has been reported within the non-Markovian regime [10].
5. Conclusions

We have observed the spectral narrowing of four-wave mixing signals for excitons in the layered semiconductor GaSe. The narrowing, which arises in the non-Markovian dephasing, has been measured by time-resolved and spectrally resolved four-wave mixing spectroscopies. From the comparison between the experimental data and the calculation based on the non-Markovian theory, the correlation time of the exciton-phonon interaction defining the non-Markovian regime is obtained as 1.1 ps.

Acknowledgments

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References

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