Transient reflectivity changes of \( \beta \)-ZnP\(_2\) exciton bands by pump–probe spectroscopy using a femtosecond laser

O. Arimoto\(^a,\)*, Y. Imai\(^a\), S. Nakanishi\(^b\), H. Itoh\(^b\)

\(^a\)Department of Physics, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan
\(^b\)Department of Advanced Materials Science, Kagawa University, Takamatsu 761-0396, Japan

Abstract

Ultrafast reflectivity changes of exciton bands in \( \beta \)-ZnP\(_2\) have been investigated by pump–probe spectroscopy using a femtosecond laser. The spectrum of the pump–probe signal shows a significant negative reflectivity change in the energy range between \( E_T \) and \( E_L \) of the 1s exciton polariton, where \( E_T \) and \( E_L \) are the transverse and longitudinal exciton energies, respectively. The reflection relaxation time is 1.1 ps near \( E_L \) and 1.7 ps near \( E_T \). These relaxation times are related to acoustic-phonon scattering of exciton polaritons. Transient reflectivity changes with a dispersion-type spectral shape are also observed at the energy where the excitonic molecule luminescence appears.

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1. Introduction

Monoclinic zinc diphosphide, \( \beta \)-ZnP\(_2\), is a II–V compound with a direct band-gap energy of 1.603 eV. It shows a very clear and well-separated Wannier exciton series of singlet and triplet systems, with a relatively large binding energy of about 40 meV, which are polarized along the \( c \)- and \( b \)-axis, respectively. Fig. 1 shows the reflection spectrum of the singlet exciton for the polarization \( E \parallel c \). \( E_T \) and \( E_L \) in the figure indicate the 1s transverse and longitudinal exciton energies, respectively. The lowest exciton state, with a resonance energy of 1.5603 eV, has a large longitudinal–transverse (L–T) splitting of 4.8 meV, giving rise to a strong polariton nature. In addition, the large exciton binding energy leads to the lowest exciton state being well isolated from higher exciton states. Therefore, \( \beta \)-ZnP\(_2\) is considered as one of the most promising candidates for a detailed investigation of exciton relaxation processes in semiconductors. We have so far extensively investigated exciton relaxation processes in \( \beta \)-ZnP\(_2\) [1–7]. In a previous paper, we reported optical dephasing of exciton polaritons as well as prominent quantum beats between free- and bound excitons by a spectrally resolved four-wave mixing (FWM) technique [7]. In order to know the population-relaxation dynamics of...
excitonsystems, we have performed, in the present study, measurements of transient reflectivity changes of the exciton bands by a spectrally resolved pump–probe method using a femtosecond laser.

2. Experimental

A single crystal of \(\beta\)-ZnP\(_2\) grown from the vapor phase was mounted on a copper cold finger in a cryostat and kept at 10 K. A cw mode-locked Ti:sapphire laser pumped by a Nd:YVO\(_4\) laser was employed as the pump and probe light sources. The pulse duration and repetition rate were about 100 fs and 76 MHz, respectively. The center energy of the laser was set at 1.557 eV with a bandwidth (FWHM) of 14 meV for excitation around the 1s exciton resonance, and also set at 1.598 eV for the excitation into higher exciton bands, as shown in Fig. 1. It is noted that the exciton binding energy is so large in \(\beta\)-ZnP\(_2\) that we can separately excite the lowest exciton and the higher excitons even under excitation with the broad-band femtosecond laser. The output from the laser was split into two beams, with the probe beam time delayed with respect to the pump beam. The pump and probe beams, both with polarization \(E_{\parallel}\), were focused onto the sample with a time delay \(\tau\). The average power of the pump beam was 1 mW while that of the probe beam was 10 \(\mu\)W with the sign of \(\tau\) defined as positive when the pump pulse precedes the probe pulse. The reflected probe light was detected by a photomultiplier using double lock-in detection. In the spectrally resolved measurements, the reflected light was dispersed through a monochromator with a spectral resolution of about 0.8 meV.

3. Results and discussion

Fig. 2 shows the pump–probe signal as a function of the delay time \(\tau\) under excitation around the 1s exciton resonance (see the dashed curve (a) in Fig. 1). This signal was not spectrally resolved. The ordinate indicates a negative reflectivity change \(-\Delta R\). As seen in the figure, the reflectivity decreases abruptly upon irradiation by the pumping-light pulse, and then recovers on a picosecond time scale accompanied by a weak modulation with a period of 0.8 ps. The signal exhibits an exponential decay for positive delays with a time constant of 1.8 ps. Hereafter we call this the reflectivity relaxation time \(T_R\). The signal also has a very slow-decaying component, whose time constant is longer than 100 ps, which is likely to be related to the luminescent lifetimes of the singlet excitons of about 1 ns [5]. It is noted that the signal has a definite intensity for negative
delay. It is presumably due to some FWM signal emitted along the direction of $(k_2 - k_1) + k_1 = k_2$, where $k_1$ and $k_2$ are wave vectors of the pump and probe beams, respectively.

In order to elucidate the origin of the reflectivity change, we spectrally resolved the pump–probe signal at $\tau = 0$ ps as shown in Fig. 3. The $\Delta R$ spectrum consists of two dominant features around 1.56 and 1.55 eV. The former signal is substantial between $E_T$ and $E_L$, which leads us to conclude that it originates from the 1s exciton polariton. It is considered that the negative reflectivity changes result from the creation of many excitons by the pump laser, leading to the suppression of exciton transitions.

The spectral shape of reflectivity changes around 1.55 eV is of the dispersion type. (Note that the ordinate is $-\Delta R$.) In $\beta$-ZnP$_2$ the luminescence from an excitonic molecule, namely a bieexciton, appears at 1.550 eV [5,8,9]. Therefore, the structure is reasonably attributed to this bieexciton transition. Excitons are created by the pump laser so that a subsequent transition that occurs from the exciton state to the bieexciton state is activated forming the transient-reflection structure of dispersion type. It should be noted that the sample crystal used in the previous FWM study shows a large reflection structure at 1.55 eV due to a bound exciton called the A-exciton [7], whereas the sample used in the present study does not show any reflection structure at 1.55 eV, indicating that there is no exciton of this extrinsic nature.

In order to know the population relaxation dynamics of exciton polaritons in detail, we measured the delay-time dependences of the pump–probe signals at various polariton energies. The results are displayed in Fig. 4. Observation energies a to d are indicated in Fig. 3. The estimated reflectivity relaxation times $T_R$ are given in this figure. We regard for simplicity $T_R$ at each energy as the population relaxation time of the exciton polariton $T_1$ at that energy. The population relaxation time becomes longer as the polariton energy becomes lower. A similar tendency was recognized for the optical dephasing of the exciton polariton $T_2$ [7]. This behaviour results from the different influence of the acoustic-phonon scattering of the polariton in the bottleneck region [7]. The same periodic modulation as the spectrally integrated signal shown in Fig. 2 is
superimposed on the decay of the pump–probe signal at \( E_L \) for positive delay. The period 0.8 ps corresponds to an energy 5 meV. The modulation possibly originates from quantum interference between the lower polariton near \( E_T \) and the upper polariton at \( E_L \), since their energy separation is approximately 5 meV, although the signal decay at \( E_T \) shows much less modulation.

Delay-time dependences of the pump–probe signals around 1.55 eV were found to be rather complex: beats with a period of 0.4 ps were observed for negative delay, while for positive delay, a beat with a period of 0.8 ps was sometimes observed depending on the energy. The two periods 0.4 and 0.8 ps correspond to energies 10 and 5 meV, respectively. The former energy nearly agrees with the energy difference between \( E_T \) and \( (E_M - E_T) \), where \( E_M (= 3.1102 \text{ eV}) \) is an energy of the excitonic molecule [8], while the latter energy is the difference between \( E_T \) and \( E_M/2 \). Therefore, there is a possibility that these beats are related to quantum interferences among exciton polarization, exciton–biexciton polarization and two-photon resonant biexciton polarization, although a full understanding of the present complex behaviour requires further investigation. We also measured the pump–probe signal for the higher exciton bands (see the dashed curve (b) in Fig. 1). It was found that the temporal behaviour is similar to that in the lowest exciton band shown in Fig. 2 except for a much slower relaxation time. The \( T_R \) in the higher exciton bands was estimated as 5.4 ps, three times longer than that in the 1s exciton region. Detailed results and discussions for the higher-exciton bands will be reported elsewhere, including their temporal behaviour around 1.55 eV.

4. Conclusion

In summary, we have investigated population-relaxation dynamics of exciton systems in \( \beta \)-ZnP\(_2\) by a pump–probe technique. Negative reflectivity changes are observed in the lowest-exciton band due to the creation of many excitons by the pump pulse. The reflectivity relaxation time \( T_R \) in the L–T gap of the polariton is longer for the lower-energy polariton, reflecting a lower rate of acoustic-phonon scattering. Furthermore, transient-reflectivity changes with a dispersion-type spectral shape are found at the energy of the biexciton luminescence, which corresponds to the transition from the lowest exciton level to the biexciton level.

References