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Intensity-dependent hot-phonon relaxation in ZnSe

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Abstract

We performed time-resolved anti-Stokes Raman-scattering experiments on ZnSe crystals using pump and probe techniques. To create non-equilibrium phonons we excited the ZnSe crystals at $\lambda = 632.8$ nm with an intense pump pulse with a pulse duration of about 4 ps, which leads to efficient two-photon absorption and therefore to the creation of free carriers. By relaxation to the band edge, the highly excited free carriers emit longitudinal optical (LO) phonons. By varying the time delay between the probe and the pump pulse, the dynamical behavior of the pump pulse-induced anti-Stokes Raman signal was studied. The results are discussed with respect to plasma effects influencing the dynamical behavior of the phonon lifetime in ZnSe. © 1997 Elsevier Science S.A.

Keywords: Alloys; Hot-phonon relaxation; Raman scattering

1. Introduction

In order to improve ZnSe-based optical devices, detailed knowledge about the transient behavior of the free carrier relaxation processes and the non-equilibrium phonon properties is necessary. Since photogenerated carriers cool under emission of longitudinal optical (LO) phonons, due mainly to Fröhlich interaction [1], the investigation of the LO-phonon relaxation is a powerful tool to study the transient behavior of the phonon system.

With time-resolved anti-Stokes Raman scattering (TRASRS) the intraband relaxation time of free carriers and the phonon lifetime could be determined. First experiments of this kind were made by von der Linde et al. [2] on GaAs samples revealing an LO phonon relaxation time of 7 ps. Other authors were able to determine decay times of germanium and $Ge_{1-x}Si_x$ alloys to 8 ps and 4–15 ps, respectively [3]. Due to the lack of efficient excitation sources providing enough excess energies to the carriers, no investigations on semiconductors with larger bandgaps were performed up to now. Knowledge about the transient phonon behavior in these materials is achieved only with coherent anti-Stokes Raman-scattering experiments (CARS), obtaining for example a dephasing time $T_2 = 44$ ps in GaP [4].

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Furthermore, it is known that higher excitation densities corresponding to a free-carrier density of about 10^{19} cm^{-3} induce a collective interaction between the carriers and the lattice, the coupled LO-phonon–plasmon modes [3,5,6]. This interaction reduces the phonon lifetime in dependence on the excitation density (as shown in [7]). With decreasing of the phonon lifetime, a typical broadening of the phonon modes and a shift to higher energies appear [3], which clearly demonstrates the renormalization of the phonon states [5,6].

Up to now, results in ZnSe about the phonon lifetime only were obtained with CARS experiments [4]. In the low-intensity regime where plasma effects could be neglected, a dephasing time of $T_2 = 9$ ps was found at 4.2 K. Increasing the temperature up to 300 K, the dephasing time decreases to $T_2 = 2$ ps. Additionally, performed line form analysis of the methods were the same [4]. Dephasing processes like phonon–phonon scattering do not influence the time constant essentially.

Therefore, our TRASRS experiments on ZnSe samples complete the knowledge about the transient behavior of the non-equilibrium phonon population. In contrast to CARS determining only the coherent lifetime T_2, TRASRS allows us to investigate the phonon population relaxation. Only in the case where no dephasing processes shorten T_2, the relation $T_2 = 2T_1$ becomes valid; thus, the two different transient experiments enable us to study the occurrence of processes destroying the coherent phonon states.

2. Experimental setup

The experimental apparatus is depicted in Fig. 1. Pulses with a duration of 4 ps at a repetition rate of 3.8 MHz were generated with a cavity-dumped dye laser (DCM special) pumped by an active mode-locked and frequency-doubled Nd:YAG laser. The average power at 632.8 nm was 170 mW.

The beam was split into equally intense pump and probe beams. By using polarization rotators, the polarization of each beam was adjusted orthogonal to the other. The probe beam with variable delay was recombined spatially with the pump beam using the second beamsplitter and focussed on the sample in the cryostat using a Labram Micro-Raman spectrometer. The temporal coincidence of the two pulses was controlled by a fast MSM-diode and a sampling oscilloscope.

The samples were ZnSe bulk crystals with (100) or (111) surfaces and thicknesses of about 2 mm. They were excited in backscattering geometry corresponding to $z(x'x')-z$ for the probe pulse and $z(y'x')-z$ for the pump pulse, so in accordance with the selection rules [8] only the probe pulse generated Stokes signal from the LO phonons.

The probe beam was scattered by the non-equilibrium phonons induced by the pump beam. By varying the time delay, the changing of the anti-Stokes Raman signal reflects the temporal behavior of the non-equilibrium phonon population. To obtain the decay constant T_1, these transients were deconvoluted with the temporal shape of the laser.

3. Results

In order to test if the anti-Stokes Raman signal does not originate from thermally excited phonons, we have taken Raman spectra from an (111) surface as shown in Fig. 2(a). Apart from the LO phonon at 258 cm^{-1}, the TO mode appears at 211 cm^{-1}. On the anti-Stokes side of the spectrum, only the LO mode is present.

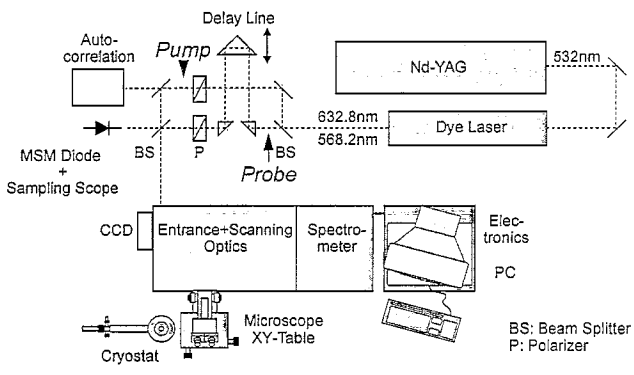

Fig. 1. Experimental apparatus for time-resolved anti-Stokes Raman-scattering.

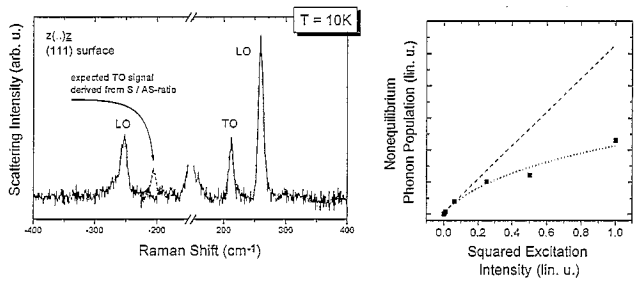

Fig. 2. (a) Stokes and anti-Stokes Raman spectra of ZnSe bulk crystal with surface orientation (111), recorded with an excitation density of about 280 MW cm^{-2}. (b) Dependence of the non-equilibrium phonon population on the squared excitation density in ZnSe. The density varies between 50 and 900 MW cm^{-2}.

In thermal equilibrium the intensity ratio of the Stokes and the anti-Stokes Raman signal is given by [8]

$$\frac{I(\omega+\Omega_S)}{I(\omega-\Omega_{AS})} \propto \exp\left(-\frac{\hbar\Omega}{k_B T}\right),$$

where Ω denotes the frequency of the Raman mode.

Under the assumption that the signal is caused by thermal phonons, the temperature derived from the ratio of the Stokes and anti-Stokes intensity of the LO mode would be about 380 K. With this temperature one can derive the expected TO anti-Stokes signal plotted in Fig. 2(a) (– – –). Because we cannot detect any TO anti-Stokes signal, it is obvious that the temperature of the sample must be much lower than the temperature derived. Fitting our data, we estimated the sample temperature to about 20 K. Therefore, effects like local heating of the sample can be ruled out and the anti-Stokes Raman signal of the LO mode arises only from the hot-carrier relaxation.

The influence of the increasing excitation density is depicted in Fig. 2(b). Under higher excitation densities, the amount of non-equilibrium phonons no

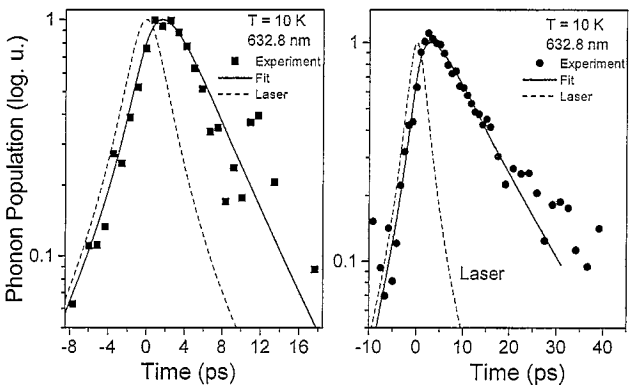

Fig. 3. (a) Time dependence of the hot-phonon population in ZnSe recorded with 280 MW cm^{-2}; (b) time dependence of the hot-phonon population in GaP recorded with 460 MW cm^{-2}.

longer depends on the squared excitation density as expected for two-photon absorption.

Fig. 3 depicts the phonon relaxation transients for GaP (a) and ZnSe (b). As shown in Fig. 2(b), at this excitation density the anti-Stokes Raman signal depends linearly on the squared excitation density, so plasma effects are negligible.

The determined time constant $T_1 = 4.5$ ps shows that the equation $T_2 = 2T_1$ is fulfilled and no dephasing processes are involved, in agreement with the CARS experiments [4].

Increasing the excitation density, the decrease of the phonon population cannot be resolved by this apparatus configuration, but the physical effect is well known: since the rate for the reabsorption of the hot phonons by the remaining free carriers is much higher than the decay of the hot phonons, the phonon population is quenched by the free carriers [9]. Additionally, the carrier–carrier scattering leads to relaxation channels other than the formation of LO phonons, and the anti-Stokes signal loses intensity significantly due to the lower amount of LO phonons created [10,11].

The phonons relaxation time of $T_1 = 11$ ps for GaP is reduced with respect to $T_2 = 44$ ps obtained with CARS, indicating the evidence of a significant hot-phonon reabsorption. It is obvious that the free-carrier concentration with respect to the lower energy gap of 2.35 eV in GaP compared with 2.82 eV in ZnSe, is significantly greater than the comparable excitation density in ZnSe.

4. Conclusions

We have performed TRASRS experiments on ZnSe crystals, which to our knowledge are the first on a broad-bandgap semiconductor, and determined the incoherent phonon lifetime to be $T_1 = 4.5$ ps at 20 K. This value supplements CARS measurements, from which one obtains a value of $T_2 = 9$ ps, indicating that dephasing processes such as phonon scattering do not occur.

In order to study the influence of the plasma effects on the phonon lifetime quantitatively, further measurements with a better temporal resolution are necessary.

References

[1] J. Collet and T. Amand, *J. Phys. Chem. Solids*, *47* (1986) 153–163.
[2] D. von der Linde, J. Kuhl and H. Klingenberg, *Phys. Rev. Lett.*, *44* (1980) 1505.
[3] J.F. Young, Kam Wan, D.J. Lockwood, J.M. Baribeau, A. Otrhonos and H.M. van Driel, *SPIE 942, Ultrafast Laser Probe Phenomena in Bulk and Microstructure Semiconductors II, 1988.*
[4] W.E. Bron, J. Kuhl and B.K. Rhee, *Phys. Rev. B*, *34* (10) (1986) 6961.
[5] M.V. Klein, B.N. Ganguly and P.J. Colwell, *Phys. Rev. B*, *6* (6) (1972) 2380;
[6] M.V. Klein, *Topics Appl. Phys.*, *8* (1975) 147.
[7] J.A. Kash and J.C. Tsang, *Solid-State Electron.*, *31* (1988) 419–424.
[8] M. Cardona, *Topics Appl. Phys.*, *50* (1982) 19.
[9] W. Pötz and P. Kocevar, *Phys. Rev. B*, *28* (1983) 7040–7047.
[10] J.A. Kash and J.C. Tsang, *Topics Appl. Phys.*, *68* (1991) 423.
[11] E.O. Göbel, *Festkörperprobleme*, *30* (1990) 270.