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2010 J. Phys.: Conf. Ser. 214 012012

(http://iopscience.iop.org/1742-6596/214/1/012012)

Journal of Physics: Conference Series **214** (2010) 012012 doi:10.1088/1742-6596/214/1/012012

Dynamics of coherent acoustic and optical phonon oscillations in nanostructures studied by a femtosecond pump-probe technique

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Abstract. Coherent phononic oscillations in Bi and Ag nanowires were studied with a femtosecond pump-probe technique. In Bi nanowires laser pulses of 50 fs excited simultaneously acoustic oscillations at a frequency of about 9.5 GHz and optical phonons in the THz range. The transmission of nanowires on a glass substrate and the light scattered from free standing nanowires were measured. In Ag nanowires laser-induced acoustic oscillations at different excitation levels were studied. The observed reduction of the oscillation frequency at higher pump energy was related to a transient softening of the material. This was directly confirmed for optical phonons by experiments with a pre-pump pulse of variable energy, producing different excitation densities.

1. Introduction

Recently, new possibilities were opened by excitation of coherent acoustic [1,2] and optical phonon [3,4] modes in different materials with short laser pulses. Such pulses excite all active vibrations, which have their frequencies contained in the pulse envelope. The laser light produces electronic excitations that are coupled to the lattice vibrations via a deformation potential and stimulated Raman scattering [5, 6]. The excitation of the lattice oscillations of optical phonons was explained via the displacive mechanism, which was shown to be related to a particular manifestation of the impulsive stimulated Raman scattering mechanism in absorbing materials. Following the action of a short laser pulse, the equilibrium positions of the nuclei are displaced, so that they start oscillating around their new equilibrium positions. Thus, laser excitation gives rise to acoustic and optical coherent phonons. Significant interest presents the application of diagnostics with short laser pulses to nanowires [7]. In nano materials the high frequency acoustic modes appear due to confinement of coherent acoustic phonons. Acoustic oscillations reflect the elastic properties, shape and dimensions of the nano-structure, while optical phonon frequencies depend on the rigidity and the effective mass of the atoms involved in the optical phonon oscillations.

Advances in generation of ultrashort laser pulses give necessary tools for the excitation of coherent acoustic and optical phonon modes in nano-materials. The laser light produces electronic excitations, which are coupled to the lattice vibrations via the deformation potential and stimulated Raman scattering.

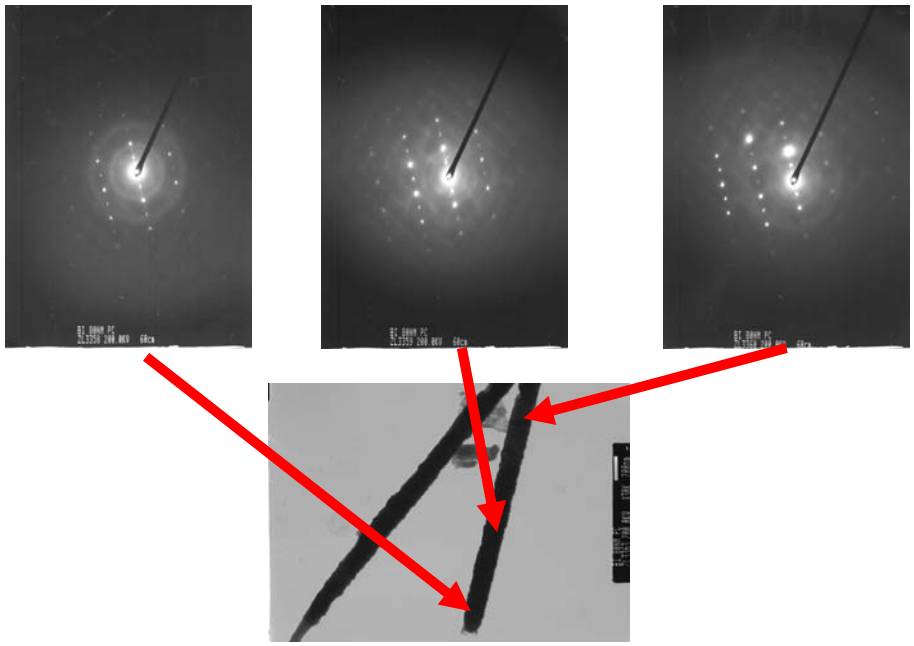

Figure. 1. The similarity of the TEM diffraction patterns (top figures) registered from different parts of a Bi nanowire (bottom figure) confirms that it consists of relatively large crystallites.

In this work we investigated optical transient responses related to coherent acoustic and optical phonons in samples of nanowires and thin films with a femtosecond pump-probe technique. The simultaneous excitation of coherent acoustic (at about 9.5 GHz) and optical phonon (in the THz range) oscillations with 50 fs laser pulses was registered in bismuth nanowires. The transmission of nanowires on a glass substrate and the light scattered from free standing nanowires were measured. In metallic materials, such as silver, plasmonic excitations strongly affect the interaction. Acoustic oscillations modulate the absorption band, and this effect can be used for the detection enhancement with a probe beam. In Ag nanowires acoustic oscillations of a breathing radial mode were observed.

Laser-induced oscillations at different excitation levels were studied. We related the observed reduction of the oscillation frequency at higher pump energies to a transient softening of the material.

2. Experimental setup

For excitation we used femtosecond laser pulses at a wavelength of 810 nm with a repetition rate of 1 kHz, and a pulse duration of about 50 fs, and for probing the pulses of the second harmonic at 405 nm were employed. The pump and probe beams were focused on the sample into spots with diameters of about 0.6 mm and 0.4 mm, respectively. The delay between the pump and probe beams was varied by a computer-controlled translation stage. The signal from a photo detector was then measured with a lock-in amplifier.

The samples of Bi and Ag nanowires were fabricated by electrochemically depositing metal into the pores of a membrane by a process described in more detail elsewhere [7]. We studied nanowires deposited on a glass substrate (the covered surface fraction was ~30 %) and also densely packed free standing nanowires. The resultant length of the nanowires was about 15 μm and the filling factor, defined as the volume fraction of the nanowires in the sample was f ~ 0.5. From TEM images the nanowire diameters were measured to be d=200±20 nm. An electron diffraction analysis of the crystalline structure showed that nanowires consisted of relatively large crystallites (see Fig. 1).

3. Results

3.1. Experiments with nanowires

The optical signal of the probe beam, scattered from a sample of free standing Bi nanowires is shown in Fig. 2. The energy of the pump pulses at the sample was set to 6 μJ, which corresponded to a fluence F = 2 mJ/cm^2. The energy of the probe pulses was 100 nJ. The observed signal (curve A) exhibited an initial peak followed by oscillations; it was fitted by the expression

$$S(t) = -A\exp\left(-\frac{t}{\tau_1}\right)\cos[2\pi ft(1+\alpha ft)+\varphi] + B\exp\left(-\frac{t}{\tau_2}\right)+C, \quad (1)$$

providing the fitting parameters: $\tau_1 = 280\text{ps}$, $f = 7.7\text{GHz}, \alpha = 0.11$, $\varphi = 0.35\text{rad}, \tau_2 = 280\text{ps}$. The initial peak was also recorded with a high temporal resolution, revealing terahertz frequency oscillations in the initial portion of the signal. These high frequency oscillations are shown in the inset in Fig. 1(a), and they are characterized by the following fitting parameters of Eq. (1) $\tau_1 = 2.3\text{ps}, f = 2.6\text{THz}, \alpha = 0.01, \varphi = 0.2\text{rad}, \tau_2 = 2.7 ps.$

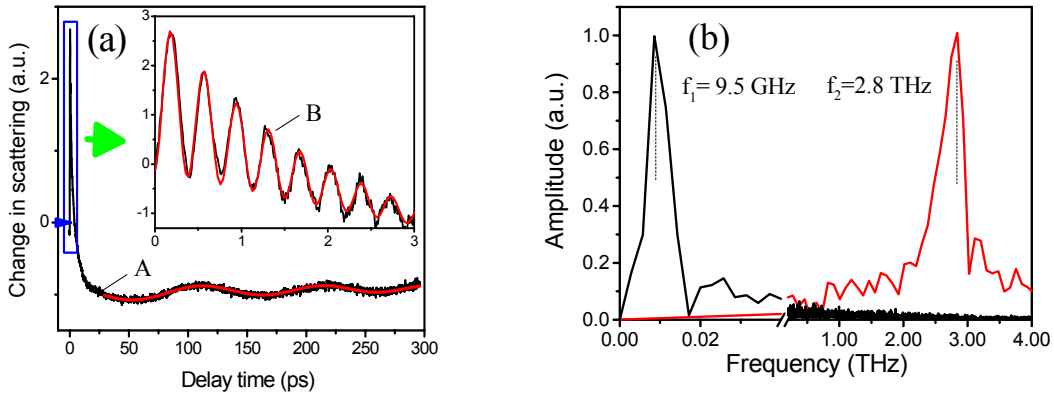

Figure 2. Transient signals of scattered light from Bi nanowires at a pump fluence of F =2 mJ/cm^2: (a) The temporal response is shown. For the signal labeled A the resolution was set to ~1 ps, and in this case acoustic phonons were detected. For curve B (inset) the resolution was set to ~100fs, and this higher temporal resolution revealed coherent optical phonon oscillations. (b) The spectral analysis of the oscillating portions of the signals A and B shows two spectral peaks with maxima at $f_1 = 9.5\text{GHz}$ and $f_2 = 2.8\text{THz}$.

The spectrum of the scattered light signals reveals an intensity modulation with two spectral peaks at $f_1 = 9.5\text{GHz}$ and $f_2 = 2.8\text{THz}$ shown in Fig. 2(b). The frequencies $f_{1,2}$ are determined by the excited coherent acoustic and optical phonons respectively. The frequency f_1 corresponds to the characteristic radial breathing acoustic mode of the nanowires $f_1 = \xi c_l / \pi d$, where the eigen number $\xi = 2.21$ is determined by the boundary problem of radial oscillations of a long rod [8]. To clarify the relative roles of different factors on the formation of the optical response related to optical phonons, we developed a model, in which electronic excitations lead to softening of the lattice and also to a transient red shift of the optical phonon frequency with the increasing density of the excitations [9].

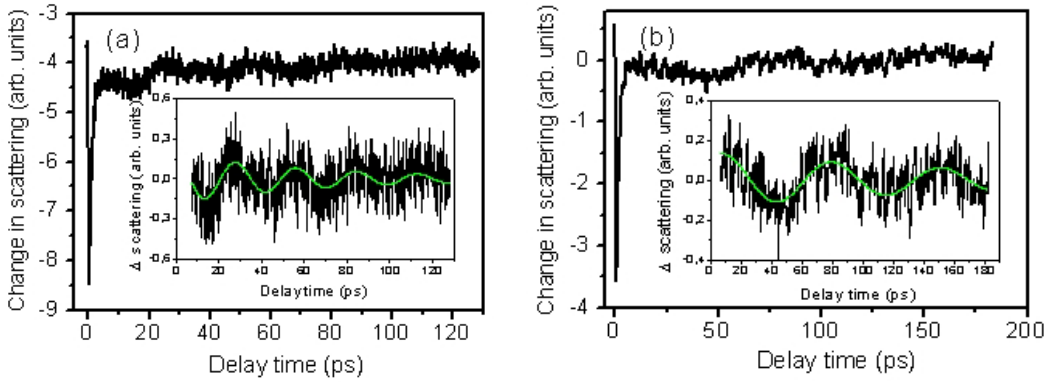

Figure 3. Transient signals measured (a) with thin (d ≈ 63 nm) Ag nanowires and (b) with thick (d ≈200 nm) Ag nanowires. Insets show the oscillating parts of the signals fitted by a damped cosine function.

For experiments with Ag nanowires, pump and probe beams of energies similar to the experiments with Bi nanowires were used: for the pump pulses the energy was about 1 μJ for the sample with thinner nanowires and 2 μJ for the sample with thicker nanowires, and for the probe pulses it was 100 nJ. The measured signals for the smaller and larger diameter Ag samples are presented in Fig.3.

The initial peak in the observed signals is related to the photo-excitation of the electonic subsystem and is followed by an oscillating signal due to the breathing acoustic mode of the nanowires. The fits in Fig.3 shown as thick solid lines correspond to a damped cosine function. From the fits, we obtain the oscillation period T = 28 ps and damping time τ = 70 ps for the smaller diameter nanowires, and T = 71 ps and τ = 190 ps for the larger diameter nanowires. For high energies of the pump pulses we observed that the period of the acoustic oscillations was changing; it was becoming larger at longer delay times and the damping time was decreasing. This can indicate a significant transient softening of the material at higher excitation levels.

3.2. Experiments with pre-pump excitation in Bi films

In order to study the effect of the level of the excitation on the optical photon frequency and the dephasing due to depth inhomogeneity of the excitation, we performed additional experiments with Bi films of about 100 nm thickness. To separate the effect of the lattice softening and the lattice anharmonicity the excitation with a pre-pump pulse was employed. This experiment is illustrated in Fig. 4, showing dependences of the probe pulse versus time delay. In Fig. 4(a) only one oscillating transient signal is present, since only the pump pulse is used for the excitation. In Fig. 4(b) two transient signals are observed when the delay of the probe pulse is varied: the first corresponds to the additional (pre-pump) pulse and the second to the pump pulse. The pre-pump pulse prepares a certain excitation state, corresponding to the laser flux used, which is then probed with the pump-probe pair of pulses. The pump pulse is sent with a small delay, when oscillations from the pre-pump pulse are almost completely damped out.

Figure 5 shows Fourier transforms of the oscillating portions of the observed probe signals. For a low laser flux of the pre-pump pulse (Fig. 5(a)) the spectrum only slightly changes, compared to the case when only the pump pulse is used for the excitation. For a high laser flux of the pre-pump (Fig. 5(b)) the peak of the spectrum is strongly shifted to lower frequencies for small delays between the pre-pump and the pump (lattice softening). Due to effects of the carrier relaxation and diffusion the peak frequency tends to restore to a higher value, and the spectrum becomes narrower with larger relative delays of the pump. Since in these experiments with a pre-pump the excitation amplitude due

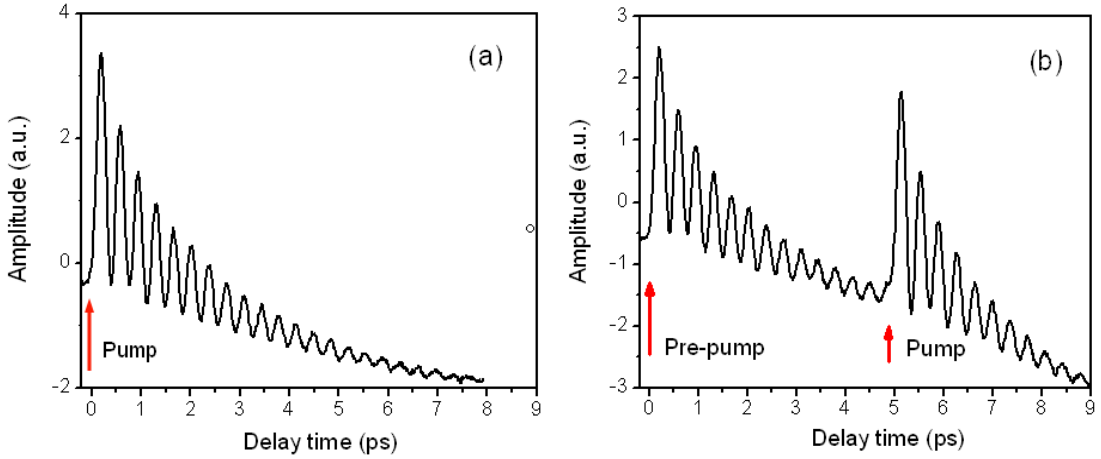

Figure 4. Temporal dependences of the signals of the reflected probe pulse on its delay time: (a) Excitation with only a pump pulse. The fluence of this pulse was fixed to 3 mJ/cm^2 for the whole series of measurements. (b) First, a pre-pump pulse is acting on the film; the flux of this pulse is varied (in the case shown it is also 3 mJ/cm^2). The pre-pump pulse is preparing a certain excitation state, which is then probed with a pair of pump-probe pulses (second oscillating trace in Fig. 4(b)). The pump is send when the oscillations induced by the pre-pump have almost vanished.

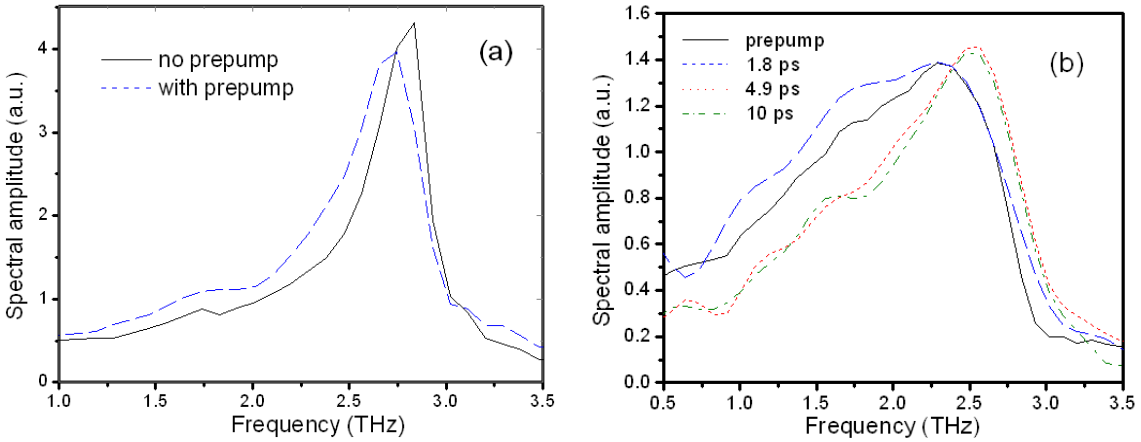

Figure 5. Spectra of the oscillating traces, corresponding to the pump pulse: (a) For signals shown in Fig. 4(a) (laser flux 3 mJ/cm^2). (b) For laser flux of the pre-pump 12 mJ/cm^2. In case (b) strong frequency shift and spectral broadening are observed for small time delays; relaxation and carrier diffusion lead to narrowing of the spectrum and an increase of the optical phonon frequency for longer delays.

to the pump is not changing much, and the frequency shift is still observed, this effect should be mainly attributed to the transient softening of the lattice, as was shown previously with a different approach, namely by varying the amplitude via interfering coherent optical phonon oscillations [10].

4. Conclusions

We observed excitation of coherent acoustic phonons in Bi and Ag nanowires and optical phonons in Bi nanowires and films after action of a short (50fs) laser pulse. It was demonstrated that such a short laser pulse can simultaneously excite acoustic (at about 9.5 GHz) and optical phonons (in the THz range) in 200nm thick Bi nanowires. In such metallic materials as silver, plasmonic excitations strongly affect the interaction. Laser-induced oscillations at different excitation levels were studied. In experiments with thin Bi films and a pre-pump pulse it was demonstrated that the observed reduction of the oscillation frequency at higher pump energies is related to a transient softening of the material.

Acknowledgments

This research is sponsored in part by the Welch Foundation, grant A-1546 and the NSF-MRI grant No.0722800.

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