# Controlling phase change through ultrafast excitation of coherent phonons

**Carl M. Liebig, Yaguo Wang, and Xianfan Xu***

*School of Mechanical Engineering and Birck Nanotechnology Center, Purdue University,*
*West Lafayette, IN 47907, USA*
**xxu@ecn.purdue.edu*

**Abstract:** For semimetals such as bismuth, ultrafast femtosecond laser-excited coherent phonons at laser fluences below the damage threshold have been studied extensively. In this work, we investigate whether or not coherent phonon oscillations contribute to material's permanent damage, or can enhance or suppress such damage. We employed temporally-shaped femtosecond pulses to either enhance or cancel coherent phonon oscillations. Our results showed a clear difference in material's damages caused by femtosecond pulses that enhance and cancel phonon oscillations, demonstrating the possibility of controlling phase changes by coherent control of phonon oscillations.

**OCIS codes:** (320.7130) Ultrafast processes in condensed matter, including semiconductors; (320.7120) Ultrafast Phenomena; (320.5540) Pulse Shaping.

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#132059 - $15.00 USD Received 21 Jul 2010; revised 2 Sep 2010; accepted 2 Sep 2010; published 10 Sep 2010

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## 1. Introduction

The ability to generate optical pulses shorter than the period of phonon vibration allows for investigations of coherent phonons in certain materials, particularly in semimetals such as bismuth [1–8]. The mechanism responsible for generating coherent phonons in opaque materials is the displacive excitation of coherent phonons (DECP) [1,2]. DECP describes exciting a large population of valence electrons to the anti-bonding conduction band, shifting the equilibrium positions of the crystal lattice, and causing atoms to vibrate around the new equilibrium position.

In this study, we investigate the effect of coherent phonon oscillation on permanent damage in bismuth. A number of studies have shown by using double-pulse excitation, the amplitude of coherent phonon oscillation can be controlled in various materials [9–11], and it was demonstrated that such coherent phonon control can be realized at laser fluences near the damage threshold [12,13]. In our earlier work, double-pulses with different pulse separation times were used to control the coherent phonon amplitude and determine the amount of energy coupled into the coherent phonon oscillation [11]. In this work, we use a temporal pulse-shaping technique to synthesize two-pulse and four-pulse pulse trains. Our objective is to control material's damage through resonantly enhancing or suppressing coherent phonon oscillations. The effect of coherent oscillations is analyzed by comparing material damages when coherent oscillations are enhanced or cancelled.

## 2. Experimental setup

The sample used in this study was a 100 nm thin-film of Bi evaporated onto a polished silicon substrate. The thickness of the film is considerably larger than the penetration depth of 800 nm and 400 nm light used in this work, which are approximately 24 nm and 15 nm respectively. The experimental setup was a collinear two-color pump-probe setup. The laser source was a Spectra-Physics Spitfire regenerative amplifier system, which produces 50 fs full-width half-maximum pulses with energies up to 200 μJ at a repetition rate of 5 kHz. The pump pulse was shaped through amplitude and phase modulation using a double 128-pixel liquid crystal spatial light modulator [14]. The frequency of the shaped pump pulse was doubled. The collinear 400 nm pump and 800 nm probe beams were focused onto the sample using a 10 cm focal length lens. The 1/e Gaussian contour diameters of the pump and probe pulses are 14.5 μm and 6.1 μm respectively. The reflected probe beam was collected using a balanced photodetector and a lock-in amplifier.

To control coherent phonon oscillations and to determine their effects on damage, pulse trains consisting of two and four pulses were designed using the pulse-shaper discussed above. When the separation time between the incident pulses matches the period of the phonon oscillation, the amplitude of coherent phonons was enhanced, whereas phonon oscillations were cancelled when the incident pulse separation corresponds to half orders of the phonon period. Due to phonon softening that occurs with increased excitation fluences, it is necessary to customize the pulse separation times for individual laser fluences. It has also been found necessary to use different pulse energy ratios in the pulse train to cancel the phonon oscillation as the vibrations decay over the time span of the pulse separations [11]. In this study, the same pulse energy ratios were used for both the pulses designed to enhance and cancel phonon oscillations at a given total laser fluence.

#132059 - $15.00 USD Received 21 Jul 2010; revised 2 Sep 2010; accepted 2 Sep 2010; published 10 Sep 2010

## 3. Results and discussion

We first discuss the results for characterizing the effects of pulse shapes on coherent phonon oscillations and for ensuring that the synthesized pulse trains can indeed enhance or cancel phonon oscillation. Figure 1(a) shows the change in reflectivity as a function of time for single pulse excitation with a fluence of 1.2 mJ/cm$^2$. Figures 1(b) and 1(c) show the results using double-pulse pulse train excitation for a total fluence of 1.2 mJ/cm$^2$. The arrows along the abscissa indicate the arrival of the excitation pulses. From Figs. 1(b) and 1(c), it can be seen that by controlling the delay time and energy ratio between the excitation pulses, the amplitude of the coherent phonon oscillations can be enhanced or cancelled. Figures 1(d) and 1(e) show the results when excited with four-pulse pulse trains, again with a total fluence of 1.2 mJ/cm$^2$. For Figure 1(e), the second pulse was designed to cancel phonon oscillations generated by the first pulse, and the fourth pulse to cancel oscillations generated by the third pulse. The separation times between the consecutive pulses in Fig. 1(d) are δT, 2δT, and δT, and in Fig. 1(e) are 1.5δT, δT, and 1.5δT (δT is the phonon oscillation period). Therefore, the total time durations are the same between the first pulse and the fourth pulse for the two cases.

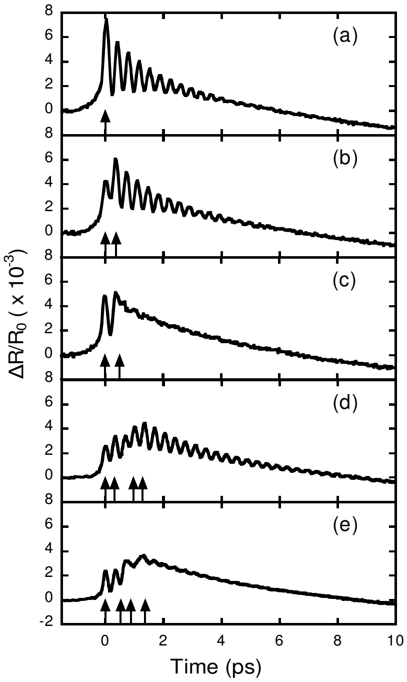

Fig. 1. Single pulse (a), double-pulse (b),(c) and four-pulse (d),(e) pump-probe measurements of reflectivity in bismuth. Shaped pulses were designed to enhance (b)(d) and cancel (c)(e) coherent phonon oscillations. The total incident fluence used in these measurements was 1.2 mJ/cm$^2$. The arrows along the x-axis show the arrival of the excitation pulses. For the double-pulse excitation, the peak amplitudes normalized to that of the first pulse are 1.0 and 0.5. For the four-pulse excitation, the peak amplitudes normalized to that of the first pulse are 1.0, 0.46, 1.05, and 0.7. The separation times between the consecutive pulses in Fig. 1(d) are δT, 2δT, and δT, and 1.5δT, δT, and 1.5δT in Fig. 1(e), where δT is the phonon oscillation period.

For 800 nm excitation, bismuth reaches the thermal melting temperature of 544 K when excited by a single pulse with a fluence of ~1.5 mJ/cm$^2$, but requires a fluence of ~4.1 mJ/cm$^2$ to melt due to the latent heat of fusion [15]. Using the melting threshold value at 800 nm and accounting for the difference in absorption using Fresnel's equations [16], the melting threshold at 400 nm is calculated to be approximately 2.6 mJ/cm$^2$. Figure 2(a) shows pump-probe measurement for single pulse excitation of bismuth at a fluence above the melting

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threshold for both short (inset) and long delay times. The arrow indicates the lowest reflectivity, representing the highest temperature reached in the process since the reflectivity of bismuth has a negative temperature coefficient [11]. Figure 2(b) shows the lowest reflectivity as a function of fluence. The lowest reflectivity changes almost linearly with the laser fluence. Similar results have also been observed when bismuth was excited above the melting threshold [4].

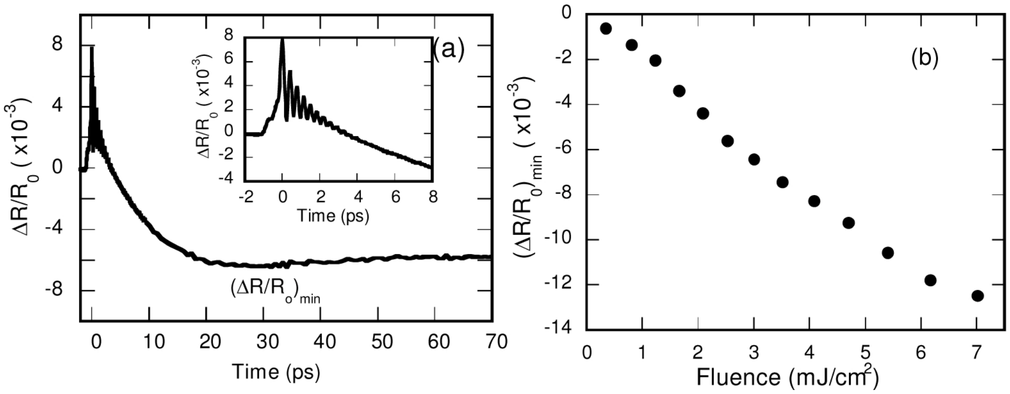

Fig. 2. (a) Pump-probe measurements for fluence of 3.1 mJ/cm$^2$ for long and (inset) short delay times. The arrow shows the time when the lowest reflectance or highest temperature is obtained. (b) The minimum reflectivity as a function of laser fluence.

The laser fluence required to cause permanent damage using a single 400 nm pulse is about 14 mJ/cm$^2$ (see below). At laser fluences above the melting threshold and up to the single-shot damage threshold, coherent oscillations can still occur in the first few picoseconds due to the time required to transfer energy from electrons to the lattice. The effect of phonon oscillations at these higher fluences on materials damage was investigated in this work. The damaged areas produced by 5,000 pulses were measured. Using 5,000 pulses instead of single pulse allows determination of the damage areas more accurately. Figure 3 shows the multi-pulse damage area as a function of laser fluence for 5,000 (a) double-pulse and (b) four-pulse excitation designed to enhance and cancel coherent phonon oscillations. It is seen that for both cases, the damage areas caused by enhanced phonon oscillations are larger than those when phonon oscillations are suppressed. An example of surface optical image produced by phonon enhancement and phonon cancellation with a total laser fluence of about 7 mJ/cm$^2$ is shown in Fig. 3(c). Experiments were repeated in each case (six times each shown in the figure) to ensure reproducibility of the results. The image shows a clear difference in the size of the damaged area between phonon enhancement and phonon cancellation. Also, the damaged area appears darker with phonon enhancement compared with that produced with phonon cancellation.

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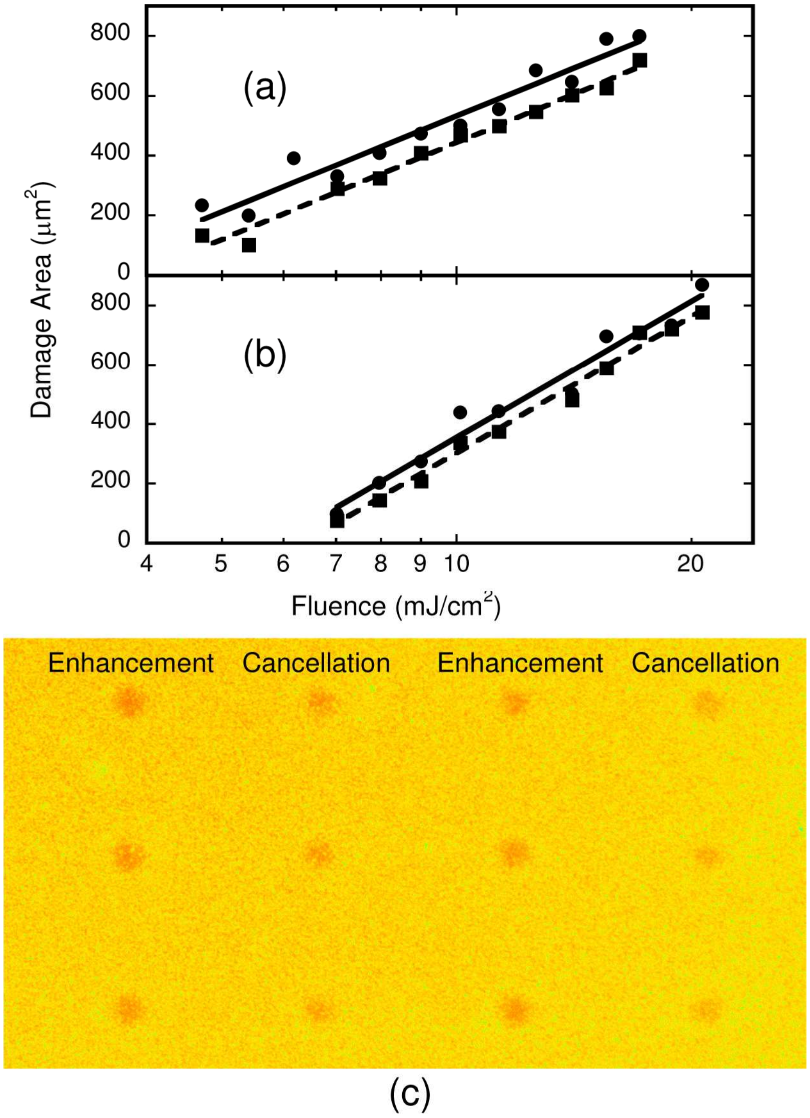

Fig. 3. Area of visible damage as a function of the incident pulse fluence for 5,000 (a) double-pulse and (b) four-pulse pulse trains designed to enhance and cancel coherent phonon oscillations. For the double-pulse, the normalized pulse amplitudes were 1.0 and 0.15 with a pulse separation of 406 fs for enhancement and 610 fs for cancellation. For the four pulse measurements the normalized pulse amplitudes were 1.0, 0.15, 1.0 and 0.15. For double-pulse excitation a minimum total fluence of 3.15 mJ/cm$^2$ and 3.85 mJ/cm$^2$ for enhancement and cancellation of phonon oscillations, respectively and for four-pulse excitation a minimum total fluence of 5.86 mJ/cm$^2$ and 6.33 mJ/cm$^2$ for enhancement and cancellation of phonon oscillations, respectively. (c) Optical image of surface damage produced by double-pulses for phonon enhancement (column 1 and 3) and phonon cancellation (column 2 and 4). The total laser fluence is about 7 mJ/cm$^2$.

The damage regression method [17] was used to extract the minimum fluence required for damage. Due to the Gaussian intensity profile of the incident beam, the damaged area increases with the natural logarithm of the total pulse fluence. When plotted on a semi-log scale, the minimum fluence required for damage can be extrapolated as the x-intercept of the fitted line. It was found for double-pulse excitation, the minimum total fluence required for damage with 5,000 pulses was 3.2 mJ/cm$^2$ for phonon enhancement and 3.9 mJ/cm$^2$ for

Received 21 Jul 2010; revised 2 Sep 2010; accepted 2 Sep 2010; published 10 Sep 2010

phonon cancellation. For four-pulse excitation, a total laser fluence of 5.9 mJ/cm$^2$ wasneeded to damage for phonon enhancement and 6.3 mJ/cm$^2$ was needed for phonon cancellation. The difference in the fluence required between the double-pulse and four-pulse excitation can be caused by the differences in the fluences of the individual pulses - the fluences of the individual pulses in the two-pulse pulse train are higher. In addition, the four-pulse excitation allows phonon oscillations to increase over the duration of the pulse train, but does not excite the same maximum phonon amplitude compared with two-pulse excitation as seen in Fig. 1.

The differences in the damage area and the minimum fluence for damage when the coherent phonon oscillations are enhanced and cancelled are indicative of the effect of the coherent phonons on materials phase change. From a phenomenological point of view, amplifying phonon oscillations decreases the stability of the lattice and assists phase change. Results shown in Fig. 3 provide experimental evidence that coherent control of phonon oscillation can affect material's damage.

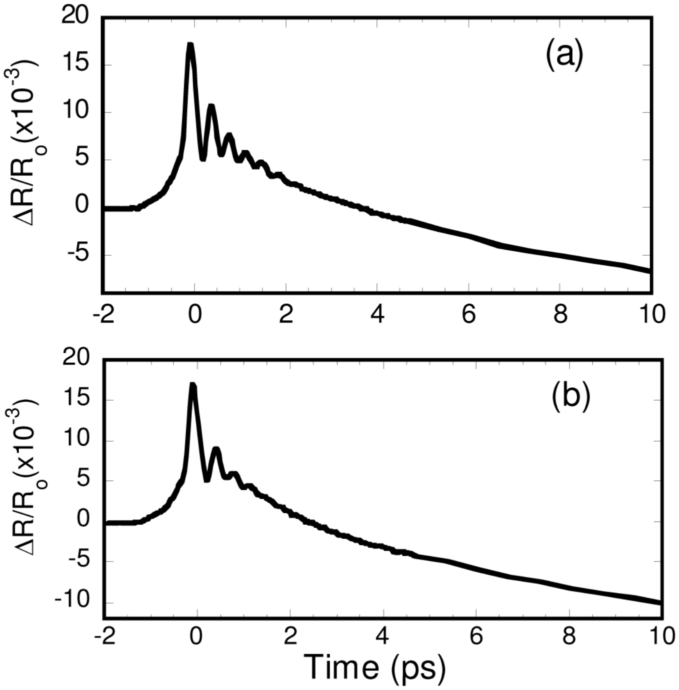

Fig. 4. Pump-probe measurements for fluences of (a) 11.3 mJ/cm$^2$ and (b) 15.6 mJ/cm$^2$ at excitation wavelength of 400 nm. Although excited at fluences close to and above the single shot damage threshold, rapidly dephasing oscillations are still visible.

We would like to point out that recent measurements using X-ray and electron diffraction have shown when the single pulse fluence is higher than 23 mJ/cm$^2$ at 800 nm excitation, "non-thermal' melting occurs at about 200 fs, faster than the coherent phonon oscillation period [18,19]. This fluence corresponds to ~14 mJ/cm$^2$ at 400 nm. For four-pulse pulse trains used in Fig. 3, the laser fluences of individual pulses are all below 14 mJ/cm$^2$. For double-pulse pulse trains, the fluence of the first pulse can be around or slightly above 14 mJ/cm$^2$ for the highest fluences used in Fig. 3 as the ratio of the first to second pulse was about 6:1, yet the phonon oscillations affect the material's damage. Phonon oscillations near and above 14 mJ/cm$^2$ were observed in our optical measurements. Figure 4 shows measurement results of a single 400 nm pulse excitation with a fluence of (a) 11.3 mJ/cm$^2$ and (b) 15.6 mJ/cm$^2$. (Since the laser fluence is close to and exceeds the single shot damage threshold, it was necessary to translate the sample during the measurement.) In our measurements, we found evidences of oscillations beyond 200 fs at fluences where "non-thermal" melting is expected. One possible reason is that in Refs. 18 and 19, the experiments were performed using thinner bismuth films

Received 21 Jul 2010; revised 2 Sep 2010; accepted 2 Sep 2010; published 10 Sep 2010

(30 nm and 50 nm) whereas in our experiments, a 100 nm-thick film was used. The thicker film in our work allows hot carriers to diffuse further away from the surface, therefore lowering the surface temperature and increasing the damage threshold.

## 4. Conclusions

In conclusion, we show that by using temporally shaped femtosecond pulse trains, we are able to control the coherent phonon oscillations in bismuth. When the pulse-to-pulse frequency of the incident pulses matches the oscillation frequency of the coherent phonons thus enhancing the amplitude of phonon oscillations, there is more damage than when the pulses cancel phonon oscillation. Therefore, controlling the coherent phonon oscillation has a direct effect on the amount of damage in materials such as bismuth.

## Acknowledgments

Support for this work by the Air Force Office of Scientific Research (AFOSR) (FA9550-08-1-0091) and the Sandia National Laboratory (No. 620550) are gratefully acknowledged. We would also like to thank Dr. Daniel E. Leaird for his insightful discussion on pulse shaping and Lin Zhao, Pornsak Srisungsitthisunti and Sreemanth Uppuluri for optical damage measurements.