PHYSICAL REVIEW B VOLUME 62, NUMBER 18 1 NOVEMBER 2000-II

Nonthermal component in heat-induced structural deformation and phase transition in gold

Chunlei Guo* and Antoinette J. Taylor
Condensed Matter and Thermal Physics Group, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 20 July 2000)

Using an ultrafast optical pump-probe technique, we study the dynamics of the heat-induced structural deformation and phase transition in gold at early time delays (within 1 ps after excitation) by monitoring both the fundamental and second-harmonic generation (SHG) signals of the probe beam. The ratios of the time-resolved fundamental and SHG signals with respect to low-intensity reference curves reveal clear changes immediately following pump excitation for intensities above 0.9× the melting threshold that is absent for lower intensities. These observations indicate a disordered lattice due to electronic heating and suggest that a nonthermal component exists in the heat-induced structural deformation and phase transition in gold.

Our understanding of femtosecond laser interactions with metals is largely based on the so-called two-temperature model.[1] An ultrashort laser pulse, with a duration less than the excited electron energy-loss lifetime, can heat electrons in a metal to a very high temperature while leaving the lattice relatively cool since the heat capacity of the electrons is much smaller than that of the lattice. Although this two-temperature model has been shown not to be strictly valid during the first few hundred femtoseconds (fs) following laser excitation,[2,3] in most cases, however, thermalization of the hot electrons can be assumed to occur instantaneously due to the short electron-electron interaction time, and therefore the overall picture of a nonequilibrium system in metals is normally described as constituting two subequilibrium systems, the hot electrons and a cold lattice.[1] This transient two-temperature system will tend to reach equilibrium within a few picoseconds (ps) through electron-phonon interactions as well as electron transport out of the excited region. In the perturbative regime, the excited region of metals will reach equilibrium with little disorder, and the dynamics of electron-electron and electron-phonon interactions in metals has been studied over the past two decades.[2–7] If the incident laser fluence is high enough to elevate the final lattice temperature to the melting point, the metal will begin a solid to liquid phase transformation. However, the understanding of the dynamics of this phase change in metals is not well understood.

The study of ultrafast melting dynamics has been vigorously pursued in semiconductors. Especially, phenomena associated with electronic-induced nonthermal melting of semiconductors have been studied systematically with a variety of semiconductor materials.[8–17] More recently, we demonstrated electronic-induced melting in a metallic system through a resonant interband excitation in aluminum.[18] Furthermore, we also investigated the conventional heat-induced melting in metals.[19,20] In Ref. 19, we study the dynamics of structural deformations and phase transitions in noble metals by monitoring the time evolution of dielectric constants: the change of the dielectric constants due to intense laser heating is relatively small at short time delays (<1 ps after laser excitation), increasing significantly at time delays longer than a few ps when the phonons become highly excited, indicative of an electronic disorder associated with lattice deformations and structural phase changes. Therefore, electronic motion plays key roles in both electronic- and heat-induced structural deformations and phase transitions in metals.[18,19] Motivated by these findings, we investigate here the possibility of electronic effects near zero pump-probe time delay, before phonons are highly excited by the hot electrons (in contrast to Ref. 19, where the time scale investigated is mainly beyond a few ps). Since the change of the dielectric constant due to structural change in heat-induced structural deformations and phase transitions is relatively small before the phonons are highly excited,[19] new techniques with higher sensitivity are needed to reveal the nature of any electronic effects at this ultrashort time scale (within 1 ps after excitation).

In this paper, we perform optical pump-probe measurements to investigate the ultrafast heat-induced structural phase change in Au at early time delays (<1 ps and before significant transfer of energy from hot electrons to lattice) by monitoring the time evolution of both the fundamental reflectivity (1.55 eV) and surface second-harmonic generation (SHG at 3.1 eV) from the probe beam. The ratios of the time resolved fundamental reflectivity and SHG signal with respect to low-intensity reference curves reveal clear changes immediately following pump excitation for pump intensities above 0.9× the permanent melting threshold (I_{th}) that is absent for intensities below $0.9I_{th}$. These observations are indicative of a disordered lattice due to electronic heating and suggest that a nonthermal component exists in the heat-induced structural deformation and phase transition in Au.

The experimental system follows the basic setup described in Refs. 18 and 19. Briefly, we perform cross-polarized optical pump-probe (p-polarization for probe) measurements using an amplified Ti:sapphire laser system running at a 1 kHz repetition rate, producing over 800 μJ/pulse in 110 fs pulses with a central wavelength of 800 nm. The repetition rate of the laser pulses can be further reduced with a pulse selector. The pump beam is weakly focused near the normal incidence onto the sample, while the probe beam, incident at 52°, is focused to an area ~ 10 times smaller than that of the pump beam to ensure probing of a uniformly excited area. Surface SHG is generated by the

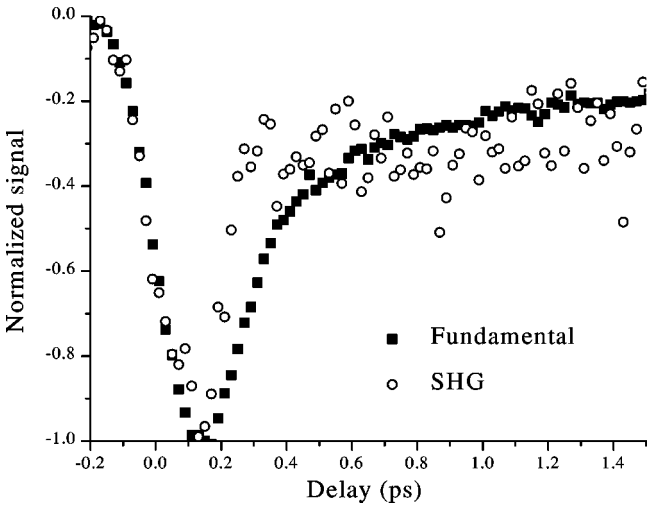

FIG. 1. A set of typical time-resolved fundamental and SHG signals for Au following pump excitation.

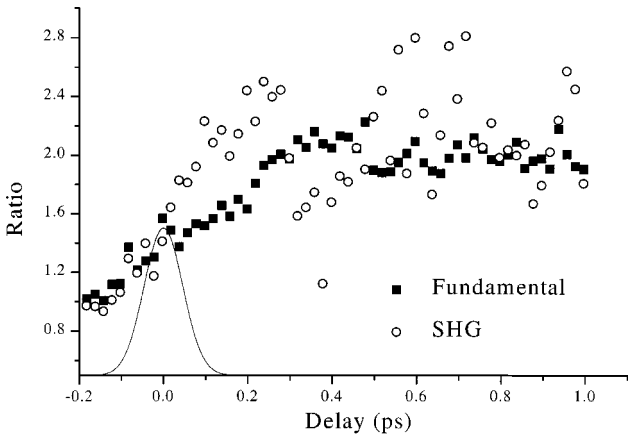

FIG. 2. Ratio curves for the fundamental and SHG signals for a pump intensity at $0.68I_{th}$ versus $0.45I_{th}$. The temporal shape of the pump pulse is plotted around the zero time delay.

weak probe beam that does not cause any modification of the sample. The collinearly propagated reflected fundamental and SHG beams are separated by a dichroic beamsplitter and monitored simultaneously. Polarizers and narrow bandpass interference filters centered at 800 and 400 nm are used for detection of the fundamental and SHG signals, respectively. An intensity window circuit is used to restrict the data collection to within a fluctuation range of 5% for a certain incident pulse energy. The Au sample used in these experiments is a polycrystalline, thick, optical film (~ 1 μm) prepared by high vacuum deposition. The sample is mounted on a high-speed and -precision motion system consisting of a rotation stage on top of a translation stage, permitting positioning of the sample to a fresh spot between laser shots.

The dynamics of the relaxation process following intense pump excitation in Au can be studied by monitoring both the fundamental and SHG signals from the probe pulse. Since the onset of major interband transition in Au (2.45 eV) exceeds the fundamental laser photon energy used in the experiment (1.55 eV), any laser-induced change in Au is expected to be predominately an ultrafast heating process.[19] Therefore, the structural change studied here in Au is a heat-induced structural deformation and phase transition,[19] which is in contrast to the electronic-induced melting in metals caused by interband excitation.[18] A set of typical time-resolved fundamental and SHG signals for Au following a pump pulse are plotted in Fig. 1. Both the fundamental and SHG signals initially decrease after pump excitation, reaching minimum values, and then recovering, consistent with previous observations that attributed the observed signals to laser heating and the ensuing relaxation due to electron-phonon coupling.[18,21] As pump intensity varies, the amplitude of the induced change in the probe signals, at both fundamental and SHG, varies at each delay time. However, the overall shape of the probe signals is qualitatively similar at different pump intensities, both above and below the damage threshold; little can be learned directly by studying only these probe traces.[22] New techniques need to be introduced to unravel the underlying electronic dynamics, if any, associated with structural change.

In order to enhance the signature of electronic effects associated with structural change, we introduce a well-established technique from the study of intensity-dependent ionization yields of atoms[23,24] and molecules[24–26] in intense laser fields based on the ratio curve of two ion yields, where a small component (e.g., nonsequential ionization component) can normally be detached from an overall ionization signal.[24] We analyze here the ratio of time-resolved fundamental reflectivity or a SHG signal at two different pump intensities. For the results discussed here, the reference traces for both the fundamental and SHG data were acquired at a pump intensity of $0.68I_{th}=1.02\times10^{12}$ W/cm^2 ($I_{th}=1.5\times10^{12}$ W/cm^2). The ratio curves are then obtained with traces at various pump intensities (both above and below the damage threshold) vs the reference traces. Note there is no particular reason to choose the reference curve at $0.68I_{th}$, the conclusions reached are qualitatively similar as long as the reference curve corresponds to an intensity below $0.9I_{th}$ (discussed later). The time-dependent ratios of the fundamental and SHG signals are plotted in Fig. 2 for a pump intensity of $0.68I_{th}$ versus $0.45I_{th}$. (Note, to be consistent, we always plot the ratio of a higher-intensity trace versus a lower-intensity trace). The ratio starts at around 1 before pump excitation, and we can see there is a smooth increase in the ratios of both fundamental and SHG due to pump excitation before a delay of $\sim$300 fs, followed by relatively constant values in the ratio curves. (Note that the relatively large changes in the SHG ratio curves at time delay $\sim$300 fs, in both Figs. 2 and 4, result from electron thermalization, which has been discussed in detail elsewhere[27] and is relatively unimportant to the major discussions in this paper). The slow increase of the ratios (mostly during the presence of laser pulses) characterizes a dynamic process of the electron response to laser heating before thermalization is reached. The ensuing relatively constant values of ratio curves indicate a similar time-dependent behavior of the induced changes at different intensities below melting. Qualitatively similar temporal behaviors are found in the ratio curves at both fundamental and SHG signals as long as the pump intensities for the numerator and denominator traces are each below $0.9I_{th}$ (discussed later).

Now we plot the ratios of the fundamental and SHG signals for pump intensities at three intensities around the melting threshold ($0.95I_{th}=1.43\times10^{12}$ W/cm^2, $I_{th}=1.5\times10^{12}$ W/cm^2, and $1.13I_{th}=1.7\times10^{12}$ W/cm^2) with re-

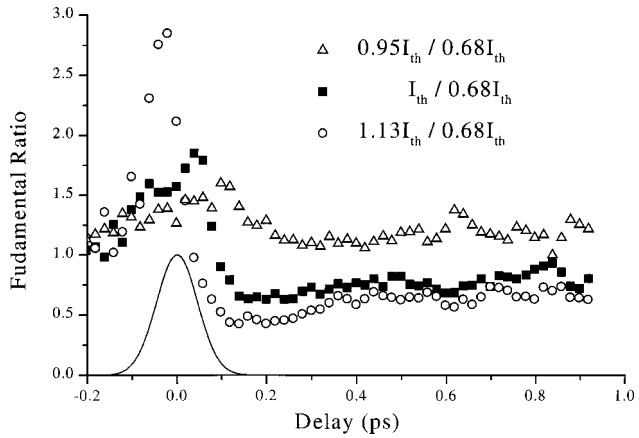

FIG. 3. Ratio curves for the fundamental reflectivity for pump intensities at $0.95I_{th}$, I_{th}, and $1.13I_{th}$ versus $0.68I_{th}$. The temporal shape of the pump pulse is plotted around the zero time delay.

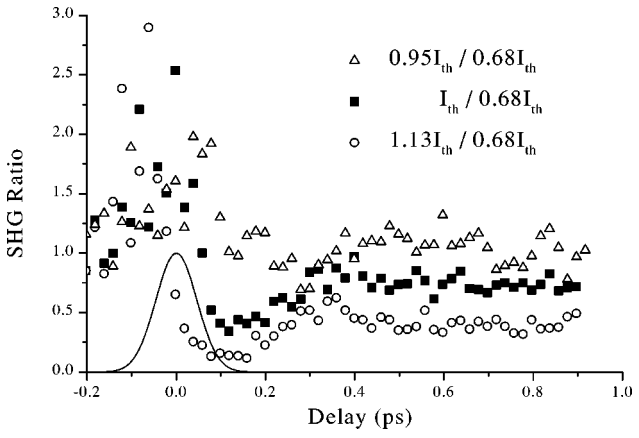

FIG. 4. Ratio curves for the SHG signals for pump intensities at $0.95I_{th}$, I_{th}, and $1.13I_{th}$ versus $0.68I_{th}$. The temporal shape of the pump pulse is plotted around the zero time delay.

spect to the same reference trace in Fig. 2 acquired at $0.68I_{th}$. These ratios are plotted in Figs. 3 (fundamental) and 4 (SHG). We can see that the ratio curves first increase at the rising edge of the pump pulse reflecting different response dynamics in Au between different intensities, as in Fig. 2. In contrast to the ratios acquired for pump intensities below $0.9I_{th}$ (Fig. 2), however, there is a clear drop in the ratio curves immediately after a zero time delay in Figs. 3 and 4. This drop shifts to an earlier delay time and the magnitude increases for higher pump intensity. Furthermore, for the same pump intensity, the drop occurs earlier in the SHG ratio (Fig. 4) than the fundamental ratio (Fig. 3). With this technique, we observe that the onset pump intensity for this ratio drop is about $0.9I_{th}$; the drop first appears in the SHG ratio curve and then in the fundamental ratio curve as intensity increases. Finally, we observe a systematic increase in the change of amplitude and a shift to an earlier time delay for the ratio drop with increasing pump intensity, indicating that this drop is caused by the pump excitation.

Since the ratio drops at high pump intensities (Figs. 3 and 4) are in distinct contrast to the slow rising of the ratios at lower intensities (Fig. 2), these drops have to be attributed to a different mechanism from that at lower intensities that are dominated by purely electronic responses. Furthermore, the fact that the ratio drops occur only at intensities close to the melting threshold strongly indicates that the ratio drops are due to lattice motion instead of purely electronic responses. However, the time scale of the ratio drops in the fundamental and SHG signals occurs within 150 fs after pump excitation, much less than the time scale of a thermal process needed to significantly transfer energy from hot electrons to the lattice in Au (at least a couple of picoseconds.[7]) Therefore, lattice disorder, if any, associated with the ratio drops appears to be directly driven by electronic motion rather than thermal heating. Unlike permanent damage, the onset pump intensity ($\sim 0.9I_{th}$) to induce the ratio drops is below the melting threshold indicating that this disorder is reversible. It is reasonable that the lattice can be transiently driven to a reversible disordered state due to strong electronic excitation before permanent thermal melting occurs, and similar phenomena and time scales have been found experimentally in semiconductors.[10,17] This transiently disordered lattice state can be formed from the constituent atoms moving away from their equilibrium positions by a substantial distance (e.g., 1/4 internuclear distance) due to electronic bond weakening induced by the strong pump. An estimation shows that it requires only a velocity of 1×10^3 m/sec for an atom to move a distance of 1/4 lattice space in Au in 100 fs, and this velocity is already comparable to vibrational velocity of lattice.[10] In fact, the atoms can move faster than vibrational velocity as the electronic bonding strength greatly changes.[10,11,18] Furthermore, the drop in signal occur faster in the surface SHG ratios (Fig. 4) than in the fundamental ratios (Fig. 3) for the same pump intensity, indicating that the disorder occurs first on the surface (probed by SHG), then moves into the bulk (probed by fundamental), consistent with the fact that the atomic bonding on surface is weaker than in bulk. These observations lead us to conclude that a nonthermal disordered lattice state exists in the structural deformation and phase transition in Au induced by ultrafast laser heating.

In summary, we have investigated the dynamics of the heat-induced structural deformation and phase transition in gold at early time delays (within 1 ps after pump excitation) by monitoring both the fundamental and SHG signals of the probe beam. The ratios of the time resolved fundamental and SHG signals with respect to low-intensity reference curves reveal clear changes immediately following pump excitation for intensities above $0.9I_{th}$ that is absent at lower intensities. These observations indicate a disordered lattice due to electronic heating and suggest that a nonthermal component exists in the heat-induced structural deformation and phase transition in Au. The findings presented in this paper provide microscopic insights to form a more complete understanding of physical mechanism of metal melting.

We acknowledge technical assistance from G. Rodriguez and J. P. Roberts. This research was supported through the Los Alamos Directed Research and Development Program by the U.S. Department of Energy.

*Electronic address: cguo@lanl.gov

[1] M.I. Kaganov, I.M. Lifshitz, and L.V. Tanatarov, Zh. Éksp. Teor. Fiz. **31**, 232 (1956) [Sov. Phys. JETP **4**, 173 (1957)].

[2] W.S. Fann, R. Storz, H.W.K. Tom, and J. Bokor, Phys. Rev. B **46**, 13 592 (1992).

[3] C.-K. Sun, F. Vallee, L. Acioli, E.P. Ippen, and J.G. Fujimoto, Phys. Rev. B **48**, 12 365 (1993).

[4] G.L. Eesley, Phys. Rev. Lett. **51**, 2140 (1983).

[5] J.G. Fujimoto, J.M. Liu, E.P. Ippen, and N. Bloembergen, Phys. Rev. Lett. **53**, 1837 (1984).

[6] H.E. Elsayed-Ali, T.B. Norris, M.A. Pessot, and G.A. Mourou, Phys. Rev. Lett. **58**, 1212 (1987).

[7] R.W. Schoenlein, W.Z. Lin, J.G. Fujimoto, and G.L. Eesley, Phys. Rev. Lett. **58**, 1680 (1987).

[8] J.A. Van Vechten, R. Tsu, and F.W. Saris, Phys. Lett. **74A**, 422 (1979).

[9] C.V. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **50**, 454 (1983); **51**, 900 (1983).

[10] H.W.K. Tom, G.D. Aumiller, and C.H. Brito-Cruz, Phys. Rev. Lett. **60**, 1438 (1988).

[11] P. Saeta, J.K. Wang, Y. Siegal, N. Bloembergen, and E. Mazur, Phys. Rev. Lett. **67**, 1023 (1991).

[12] D.H. Reitze, H. Ahn, and M.C. Downer, Phys. Rev. B **45**, 2677 (1992).

[13] L. Huang, J.P. Callan, E.N. Glezer, and E. Mazur, Phys. Rev. Lett. **80**, 185 (1998).

[14] K. Sokolowski-Tinten, J. Bialkowski, M. Boing, A. Cavalleri, and D. von der Linde, Phys. Rev. B **58**, R11 805 (1998).

[15] K. Sokolowski-Tinten, J. Solis, J. Bialkowski, J. Siegel, C.N. Afonso, and D. von der Linde, Phys. Rev. Lett. **81**, 3679 (1998).

[16] C.W. Siders, A. Cavalleri, K. Sokolowski-Tinten, Cs. Tóth, T. Guo, M. Kammler, M. Horn von Hoegen, K.R. Wilson, D. von der Linde, and C.P.J. Barty, Science **286**, 1340 (1999).

[17] A.H. Chin, R.W. Schoenlein, T.E. Glover, P. Balling, W.P. Leemans, and C.V. Shank, Phys. Rev. Lett. **83**, 336 (1999).

[18] C. Guo, G. Rodriguez, A. Lobad, and A.J. Taylor, Phys. Rev. Lett. **84**, 4493 (2000).

[19] C. Guo and A.J. Taylor, Phys. Rev. B **62**, 5382 (2000).

[20] S. Williamson, G. Mourou, and J.C.M. Li, Phys. Rev. Lett. **52**, 2364 (1984).

[21] J. Hohlfeld, D. Grosenick, U. Conrad, and E. Matthias, Appl. Phys. A: Mater. Sci. Process. **60A**, 137 (1995).

[22] E.N. Glezer, Y. Siegal, L. Huang, and E. Mazur, Phys. Rev. B **51**, 6959 (1995).

[23] B. Walker, B. Sheehy, L.F. DiMauro, P. Agostini, K.J. Schafer, and K.C. Kulander, Phys. Rev. Lett. **73**, 1227 (1994).

[24] C. Guo, M. Li, J.P. Nibarger, and G.N. Gibson, Phys. Rev. A **58**, R4271 (1998).

[25] C. Guo, M. Li, and G.N. Gibson, Phys. Rev. Lett. **82**, 2492 (1999).

[26] C. Guo, M. Li, J.P. Nibarger, and G.N. Gibson, Phys. Rev. A **61**, 033 413 (2000).

[27] C. Guo, G. Rodriguez, M.A. Hoffbauer, and A. J. Taylor (unpublished).