

Time-Resolved Laser-Induced Phase Transformation in Aluminum

S. Williamson and G. Mourou

Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14623

and

J. C. M. Li

Department of Mechanical Engineering, University of Rochester, Rochester, New York 14623

(Received 19 March 1984)

The technique of picosecond electron diffraction is used to resolve in time the laser-induced melting of thin aluminum films. It is observed that under rapid heating conditions, the long-range order of the lattice subsists for lattice temperatures well above the equilibrium point, indicative of superheating. The melting time is found to vary according to the degree of superheating. The initial density of nuclei is determined under the assumption of a two-dimensional expansion model. These results show for the first time the relationship between superheating and the rate of transformation.

PACS numbers: 64.70.Dv, 61.41.Fe, 68.90.+g

Phase transformation in condensed matter is an important area of study in solid state physics since it relates to the genesis and evolution of new microstructure. The mechanisms responsible in such critical phenomena are still not fully understood. Previous experimental information has left unmeasured such important parameters as the minimum number of nuclei and their common critical radius for a transformation to occur as well as the interphase velocity. The short-pulse laser has become a valuable tool serving many functions in this field. Energies large enough to melt (or even vaporize) condensed substances can now be applied in a time interval much shorter than the time for the transformation to take place. Several probe techniques have now been developed to provide time resolution of phase transformations in semiconductors during laser annealing. However, most of these probes (e.g., electrical conductivity,^{1,2} optical reflection,^{3,4} optical transmission,⁵ Raman scattering,⁶ and time-of-flight mass spectrometry⁷) supply no direct information about the atomic structure of the material. Probing the structure can reveal when and to what degree a system melts as melting is defined by degradation in the long-range order of the lattice. True structural probes based on x-ray⁸ and low-energy electron⁹ diffraction and extended x-ray absorption fine structure¹⁰ with nanosecond time resolution have been developed offering fresh insight into both the bulk and surface dynamics of material structure. Also, a subpicosecond probe based on structure-dependent second-harmonic generation¹¹ has been demonstrated. But at present, only the technique of picosecond electron diffraction¹² can produce an unambiguous picture

of the structure on the picosecond time scale. In this Letter we report on the results of using this probe to observe directly the laser-induced melting of aluminum.

The technique takes advantage of the strong scattering efficiency of 25-keV electrons in transmission mode to produce and record a diffraction pattern with as few as 10^4 electrons in a pulse of 20-ps duration. The burst of electrons is generated from a modified streak camera that, via the photoelectric effect, converts an optical pulse to an electron pulse of equal duration.¹³ Equal in importance is the fact that the electron pulse can be synchronized, with picosecond resolution, to the laser pulse.¹⁴ The experimental arrangement is illustrated in Fig. 1. A single pulse from an active-passive mode-locked Nd³⁺-doped yttrium aluminum garnet laser is spatially filtered and amplified to yield energies up to 10 mJ. The streak tube (deflection plates removed), specimen, and phosphor screen are placed in vacuum at 10^{-6} mm Hg. The electron tube is comprised of the photocathode, extraction grid, focusing cone, and anode. A gold photocathode is used to permit the vacuum chamber to be opened to air. The photocathode is held at the maximum voltage (-25 kV) so that space charge, which can cause significant temporal broadening, is minimized. The portion of the laser irradiating the photocathode is first up-converted to the fourth harmonic of the fundamental wavelength in order to produce the electrons efficiently. The duration of the uv pulse and thus the electron pulse is ~ 20 ps. Once the electron pulse is generated it accelerates through the tube past the anode and then remains at a constant velocity. The specimen is lo-

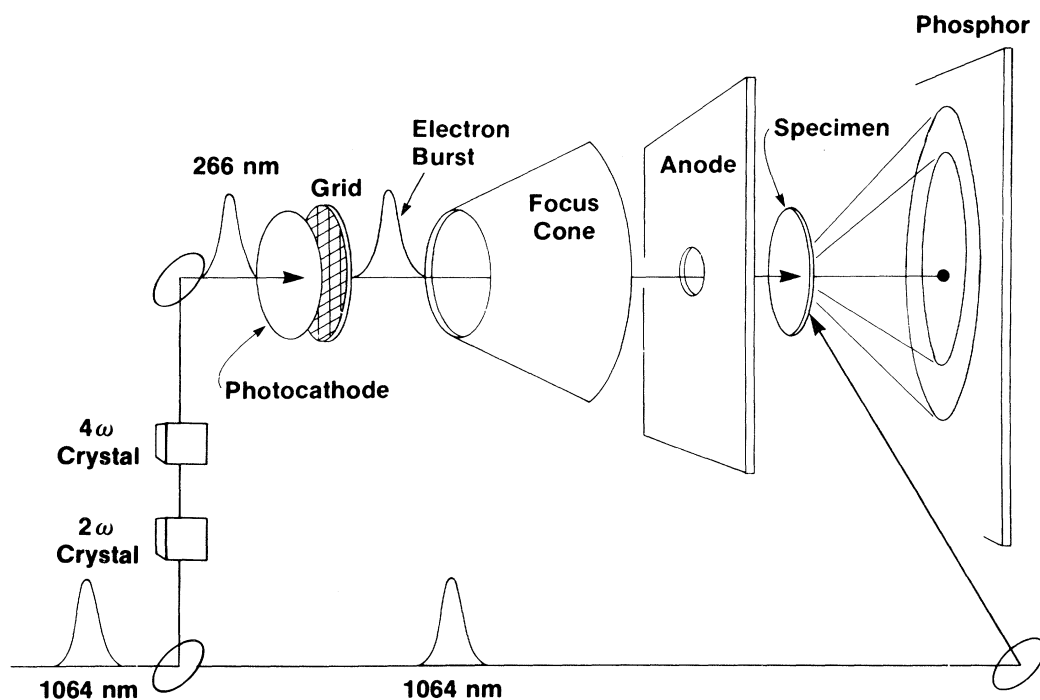


FIG. 1. Schematic of picosecond electron-diffraction apparatus. A streak-camera tube (deflection plates removed) is used to produce the electron pulse. The 25-keV electron pulse passes through the Al specimen and produces a diffraction pattern of the structure with a 20-ps exposure.

cated in this drift region. The electrons pass through the specimen with a beam diameter of $500\text{ }\mu\text{m}$ and come to a $200\text{-}\mu\text{m}$ focus at their diffracted positions on the phosphor screen. A gated microchannel-plate image intensifier in contact with the phosphor screen amplifies the electron signal $\sim 10^4$ times.

A metal was chosen over a semiconductor as the specimen because of the ease with which metals can be fabricated in ultrathin polycrystalline films. The specimens were fabricated by first depositing Al onto Formvar substrates and then vapor-dissolving away the Formvar. Free-standing films $250 \pm 20\text{ }\text{\AA}$ in thickness were required so that the electrons sustain, on the average, one elastic collision while passing through the specimen. This thickness of Al corresponds to twice the $1/e$ penetration depth at 1060 nm . It is worth noting that the penetration depth for a metal does not vary significantly from solid to liquid as is the case with a semiconductor where a change in absorption of one to two orders of magnitude is possible. Since the diffusion length $(D\tau)^{1/2}$, where D is the thermal diffusivity coefficient ($0.86\text{ cm}^2/\text{s}$) and τ is time, is limited to $250\text{ }\text{\AA}$, the temperature in the Al is uniformly established in less than 10 ps . The absorption of the laser by aluminum is $(13 \pm 1)\%$.

Since the diffracted electrons lie in concentric rings at discrete radii from the zero order we can take a circular average to enhance the signal. This is accomplished by rapidly spinning the photograph of the signal about its center. The process acts to accentuate the real signal occurring at fixed radii while smoothing out the randomly generated background noise.

The diameter of the laser stimulus is $\sim 4\text{ mm}$ ($1/e^2$) and is centered over the 2-mm specimen. A 1-mm pinhole positioned in place of the specimen facilitates accurate alignment of the laser-beam profile to the electron beam. Using a 1-mm pinhole assures accurate measurement of the fluence within the probed region. Synchronization between the electron pulse and the laser stimulus is then accomplished by means of a laser-activated deflection-plate assembly.¹⁵

The experimental procedure is then to stimulate the aluminum sample with the laser while monitoring the lattice structure at a given delay. The films are used only once even though for low fluence levels ($\leq 8\text{ mJ/cm}^2$) the films could survive repeated shots. Figure 2 shows the time-resolved laser-induced phase transformation of aluminum at a constant fluence of $\sim 13\text{ mJ/cm}^2$. The abrupt disappearance of rings in the diffraction pattern oc-

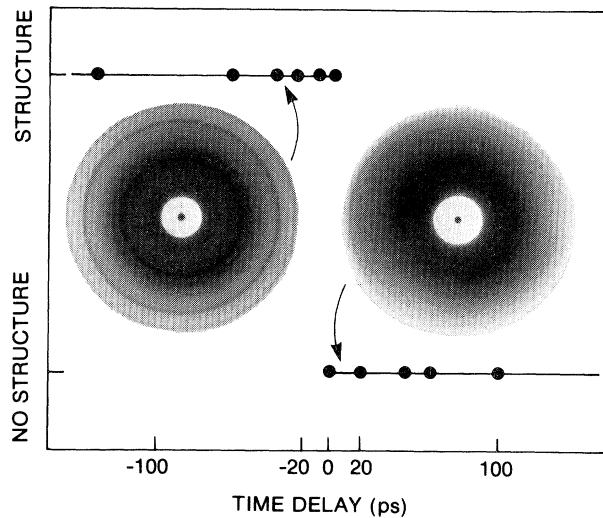


FIG. 2. Time-resolved laser-induced phase transition in aluminum. The pattern on the left is the diffraction pattern for Al and represents the points along the top line—where the electron pulse arrives before the laser stimulus. The pattern on the right shows the loss of structure in the Al 20 ps (or more) after applying the laser stimulus at a fluence of 13 mJ/cm². The fine-line background structure occurring in both pictures is an artifact of the circular averaging technique.

curs with a delay of 20 ps. As is evident, the breakdown of lattice order can be induced in a time shorter than the resolution of our probe. However, the fluence required for this rapid transition exceeds F_{melt} , the calculated fluence required to melt the Al specimen completely under equilibrium conditions (~ 5 mJ/cm²). At a constant fluence of 11 mJ/cm² the phase transition was again observed but only after a probe delay of 60 ps. Figure 3 shows the melt metamorphosis of Al where the points represent the delay time before the complete phase transition is observed for various fluence levels. We see that the elapsed time increases exponentially with decreased fluence and at 7 mJ/cm² the delay is ~ 1 ns. Because the fluence level that is applied is always in excess of F_{melt} , the observed delay time suggests that the Al is first driven to a superheated solid state before melting. It must be pointed out that as the fluence was decreased the abruptness with which the rings disappeared became less dramatic. Consequently, determination of the precise delay increases in difficulty with decreasing fluence. The temperature scale represents the temperature of the superheated Al on the assumption of a linear increase in the specific heat with temperature. We see that temperatures in excess of 2000 K are expected with fluence levels near

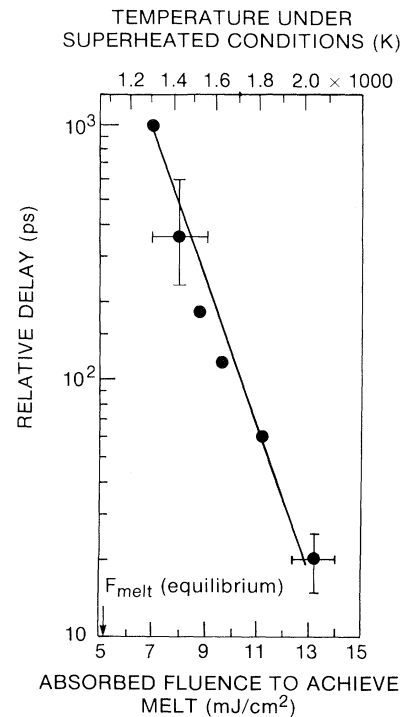


FIG. 3. Laser-induced melt metamorphosis for aluminum. The points mark the elapsed time for the diffraction rings to completely disappear. The vertical error bar represents the degree of uncertainty in defining the moment of complete melting. The region beneath the curve represents the conditions under which the Al is left in a superheated solid state.

13 mJ/cm². The region beneath the curve represents the conditions under which the Al can be observed in a superheated solid state.

Let us consider the melt to originate from a spherical cluster of atoms that begin to vibrate incoherently to the point where structural order is lost. The nucleation theory then tells us that beyond a critical radius r^* , the sphere will rapidly expand throughout the volume until the entire Al specimen is transformed into the liquid phase. The critical radius r^* is given by

$$r^* = 2\gamma_{ls}/(F_s - F_l),$$

where γ_{ls} is the interfacial free energy between the solid and liquid phases, and F_s and F_l are the free energy of each phase. An estimate of the critical radius is a few angstroms at 1500 K and a few tens of angstroms at 1000 K. According to the theory, the observed transition time (τ_{ob}) between the driving pulse and the complete disappearance of the diffraction rings should correspond to the time necessary for the expanding liquid spheres to fill the volume

between nuclei. The average distance between nuclei is $2v\tau_{ob}$, where v is the radial rate of expansion.

If we take $v = 5 \times 10^5$ cm/s and $\tau_{ob} = 20$ ps, this distance is 2000 Å, a value much larger than the film thickness. Hence, the expansion is primarily cylindrical rather than spherical. The density of nuclei is thus given by

$$N = 1/\pi(2v\tau_{ob})^2. \quad (1)$$

Equation (1) is valid regardless of whether the nuclei originate on the surface or in the bulk. If we assume v to be constant with lattice temperature, we find that the density of nuclei increases from 10^5 to 10^9 cm $^{-2}$ when the fluence is increased from 7 to 13 mJ/cm 2 . From this interpretation, it is clear to see why determining the transition time becomes increasingly more difficult with decreasing fluence. The point in time where the diffraction rings have degraded to half normal intensity is reached just a few picoseconds prior to the full melt when the fluence is 13 mJ/cm 2 but a few hundred picoseconds prior to the full melt when the fluence is 7 mJ/cm 2 .

In conclusion, we have demonstrated that the picosecond electron-diffraction technique can be used to provide time resolution of the laser-induced melt metamorphosis in aluminum. It was found possible to melt the aluminum completely in a time shorter than 20 ps if sufficient laser fluence is applied ($\geq 2.6 \times F_{melt}$). The time required to melt the aluminum increases exponentially with decreasing fluence and at $1.4 \times F_{melt}$ the phase transition time increases to ~ 1 ns. During this time, the two phases coexist as a heterogeneous melt while the superheated solid is being continuously transformed into liquid. In the future, we intend to measure directly the degree of superheating endured by the lattice by measuring the change in the diffraction ring diameters. We believe that these results show for the first time in an unambiguous way the relationship between superheating and delayed melting and demonstrate the important role that the technique of picosecond electron diffraction can play in the study of the genesis of melting.

This work was partially supported by the Laser Fusion Feasibility Project at the Laboratory for Laser Energetics which has the following sponsors:

Empire State Electric Energy Research Corporation, General Electric Company, New York State Energy Research and Development Authority, Northeast Utilities Service Company, Southern California Edison Company, The Standard Oil Company (Ohio), and the University of Rochester.

We would like to acknowledge the support of Jerry Drumheller who assisted in the fabrication of the Al films as well as to thank Hsiu-Cheng Chen for her help during the experiment.

¹M. Yamada, H. Kotani, K. Yamazaki, K. Yamamoto, and K. Abe, J. Phys. Soc. Jpn. **49**, 1299 (1980).

²G. J. Galvin, M. O. Thompson, J. W. Mayer, R. B. Hamond, N. Paulter, and P. S. Peercy, Phys. Rev. Lett. **48**, 33 (1982).

³D. H. Auston, C. M. Surko, T. N. C. Venkatesan, R. E. Slusher, and J. A. Golovchenko, Appl. Phys. Lett. **33**, 437 (1978).

⁴C. V. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **50**, 454 (1983).

⁵J. M. Liu, H. Kurz, and N. Bloembergen, Appl. Phys. Lett. **41**, 643 (1982).

⁶H. W. Lo and A. Compaan, Phys. Rev. Lett. **44**, 1604 (1980).

⁷A. Pospieszczyk, M. A. Harith, and B. Stritzker, J. Appl. Phys. **54**, 3176 (1983).

⁸B. C. Larson, C. W. White, T. S. Noggle, and D. Mills, Phys. Rev. Lett. **48**, 337 (1982).

⁹R. S. Becker, G. S. Higashi, and J. A. Golovchenko, Phys. Rev. Lett. **52**, 307 (1984).

¹⁰H. M. Epstein, R. E. Schwerzel, P. J. Schwerzel, P. J. Mallozzi, and B. E. Campbell, J. Am. Chem. Soc. **105**, 1466 (1983).

¹¹C. V. Shank, R. Yen, and C. Hirliman, Phys. Rev. Lett. **51**, 900 (1983).

¹²G. Mourou and S. Williamson, Appl. Phys. Lett. **41**, 44 (1982).

¹³D. J. Bradley and W. Sibbett, Appl. Phys. Lett. **27**, 382 (1975).

¹⁴G. Mourou and W. Knox, Appl. Phys. Lett. **36**, 623 (1980).

¹⁵S. Williamson, G. Mourou, and S. Letzring, in *Proceedings of the Fifteenth International Congress on High Speed Photography*, edited by L. L. Endelman, SPIE Vol. 348 (Society of Photo-Optical Instrumentation Engineers, Bellingham, Washington, 1983), Pt. I, p. 197.

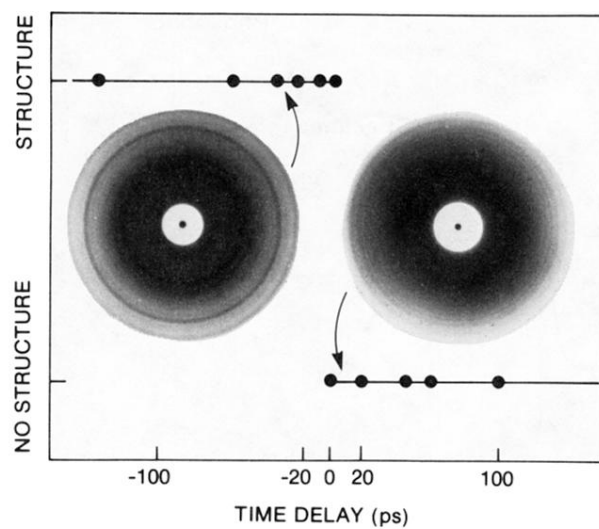


FIG. 2. Time-resolved laser-induced phase transition in aluminum. The pattern on the left is the diffraction pattern for Al and represents the points along the top line—where the electron pulse arrives before the laser stimulus. The pattern on the right shows the loss of structure in the Al 20 ps (or more) after applying the laser stimulus at a fluence of 13 mJ/cm^2 . The fine-line background structure occurring in both pictures is an artifact of the circular averaging technique.