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X-Ray Scattering Applications Using Pulsed X-Ray Sources

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ABSTRACT

Pulsed x-ray sources have been used in transient structural phenomena investigations for over fifty years; however, until the advent of synchrotron sources and the development of table-top picosecond lasers, general access to high temporal resolution x-ray diffraction was relatively limited. Advances in diffraction techniques, sample excitation schemes, and detector systems, in addition to Increased access to pulsed sources, have led to what is now a diverse and growing array of pulsed-source measurement applications. A survey of time-resolved investigations using pulsed x-ray sources is presented and research opportunities using both present and planned pulsed x-ray sources are discussed.

1. INTRODUCTION

Pulsed sources of x-rays has been developed using high current discharges, high power pulsed-lasers, pulsed-laser stimulated x-ray diodes, inverse Compton scattering of short laser pulses, and synchrotron storage rings. These sources have provided experimental access to transient structural properties of materials including deformation during shock loading, rapid laser heating and melting, and photo-induced chemical, electrical, and crystallographic changes. In addition, they have provided new access to the dynamics of materials through the use of synchrotron based time-domain nuclear resonance spectroscopy techniques. Uniform stimulation of transient phenomena with high temporal precision, without otherwise changing the overall state (e.g. such as heating) of the system under investigation and the development of high temporal resolution time-slicing detectors continue to be formidable tasks.

Synchrotron x-ray pulses are typically in the 50–200 ps range, and laser based techniques such as pulsed-laser plasma and inverse Compton scattering have now demonstrated the ability to produce x-ray pulses in the 100 fs range; and projections for so-called fourth-generation free electron laser sources indicate the possibility of femtosecond scale pulses with peta-watt peak powers. Although the ability of samples to withstand the probing x-ray pulses is a question in some cases, such sources will provide access to entirely new classes of investigation, including weakly scattering transient inelastic processes and phenomena that cannot be cycled and must be fully measured with a single pulse. In this paper, pulsed x-ray sources and detection schemes will be reviewed briefly, and a selective survey of present and projected transient phenomena investigations using pulsed time-structure x-ray sources will be presented.

2. PULSED TIME-STRUCTURE X-RAY SOURCES

Many aspects of time-resolved x-ray diffraction have been addressed in *Time-Resolved Diffraction,* as edited by Helliwell and Rentzepis.[1] Whitlock and Wark[2] recounted the development and application of high temporal resolution pulsed source x-rays beginning with the generation of millisecond x-ray pulses by Tsukerman and Avendeenko[3] in the early 1940's. The time-line in Fig. 1, indicates a 25-year resolution plateau in the nanosecond range diffraction measurements.[2] Nanosecond measurements were initiated in connection with the generation of ~50 ns x-ray pulses in 1967 by Johnson[4] et al, and extended using laser-plasma x-ray sources with high powers and small source size. Laser-plasma x-ray sources were developed[5,6] in the 1970's and applied in particular to investigations of shock loading.[7] The inherent ~150 ps pulse width and < 1 μs pulse spacing of synchrotron x-ray sources were exploited in the early 1980's in nanosecond resolution investigations of pulsed laser melting and regrowth in semicaonductors[8] As picosecond lasers were applied and table-top-tera watt (TTT) laser x-ray diode sources were developed, a rapid increase in time-resolution of x-ray scattering studies occured during the late 80's and 1990's.

Laser plasma x-ray sources with ~100 femtosecond time structures have been developed[9], and ~300 femtosecond x-ray pulses have been demonstrated in the hard x-ray regime using inverse Compton scattering from high energy electron beams.[10] The inverse Compton (up-scattering) of ~100 femtosecond lasers pulses results in the emission of femtosecond range x-ray pulses with tens of keV energies. Measurements reported in 1996 demonstrate[10, 11] the generation of 5×10^4 photons in a

~0.5 degree angular width pulses. The intensity per pulse from inverse Compton scattering is is not large by present synchrotron source standards, and considering the wide angular dispersion, the pulses would be rather weak for high angular resolution diffraction experiments. However, optimization techniques exist that could improve this number dramatically.

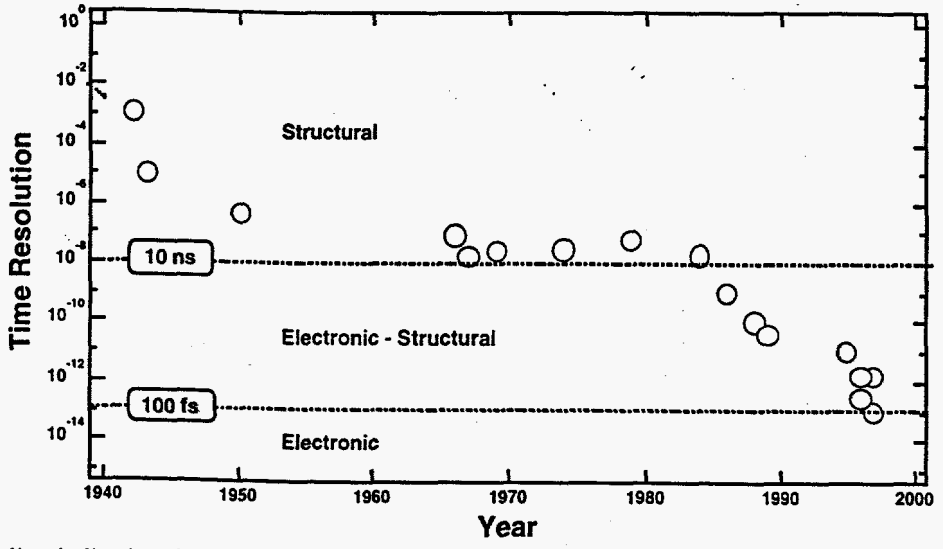

Fig. 1. Time-line indicating the development of high-resolution time-resolved x-ray diffraction measurements.

Free electron lasers with 1 Å wavelengths are of course not near a demonstration at present, but, projections for these so-called fourth-generation sources indicate the possibility of ~300 fs x-ray pulses with power capable of vaporizing highly absorbing samples. Peak brilliance (ph/(s-st-area-bandwidth)) is projected[12] to be about 10 orders of magnitude higher than third generation synchrotron sources, and calculations indicate 2×10^{12} photons/pulse at 1.5Å with a transverse size of 80 microns, 277 fs time duration, and 0.2 arcsec divergence. These projections of 2.5 mJ/ pulse correspond to 2500 J/cm^2 if focused onto a 0.1×0.1 mm^2 area. Therefore, depending on the absorption characteristics of individual cases, sample pumping as well as diffraction can be considered with the available photons.

Nanosecond resolution provided access to fast transient structural phenomena and picosecond range resolution has led to investigtions involving electronic-structural interactions. The development of femtosecond x-ray pulses will provide access to the frequency range of single atom motions and elementary processes of diffusional motion, and to the study of electronic processes involved in chemical reactions. Femtosecond measurements will include information on nuclear coordinates and dynamics as well as information on electronic states that is complementary to laser spectroscopy information generated by optical wavelength pulsed laser studies. Femtosecond resolution x-ray measurements present formidable challenges, however, the prospect of fundamentally new information on elementary processes associated with phenomena ranging from solid state physics to molecular biology will drive the development of the needed instruments and measurement techniques.

3. PULSED TIME-STRUCTURE X-RAY DETECTORS

In considering the detection requirements of short x-ray pulses for time resolved investigations, the ability to control the delivery rate of short pulses is as important as the actual production of the pulses. The production of continuous (x-ray or optical) sources with terawatt power levels would be neither desirable from the standpoint of dissipating the energy, nor would it be feasible from the standpoint of producing such high power levels. Furthermore, continuous sources place the entire burden of high resolution synchronization and time-slicing on the detection system. In all but the most simple of detection schemes, recovery and resetting of detectors (after scattering events from previous pulses) and the synchronization of multi-element detector arrays would be completely out of the realm of possibility.

Although no longer the detector of choice in most cases, wet-film has been an exceptional medium for x-ray detection, and it has played an important role in time-resolved as well as static x-ray measurements. In their nanosecond resolution shock loading measurements, Johnson[4] et al employed separate scintillation detectors, but relied on film for higher resolution measurements. Film attributes include high spatial resolution, photon integration, two-dimensional detection, and very low

cost. Film limitations are dynamic range and speed of handling data extraction; the development of x-ray image plates and large CCD detectors are largely replacing wet film as a detection medium.

Mechanical shutters can be employed to limit exposure to single x-ray pulses in the presence of a a continuous stream of pulses, even in the case of single bunch ~microsecond repetition rates at synchrotrons, as illustrated in Fig. 2. This scheme was utilized[13] in connection with single shot white beam Laue crystallography at CHESS. The technique is of course effective with CCDs as well; the present status of developments in this area have been reviewed by Wulff[14] et al. Techniques have been developed at ESRF to synchronize the speed of the mechanical chopper to the synchrotron ring frequency to get greater throughput when multiple exposures (different from the x-ray pulse frequency) are required.

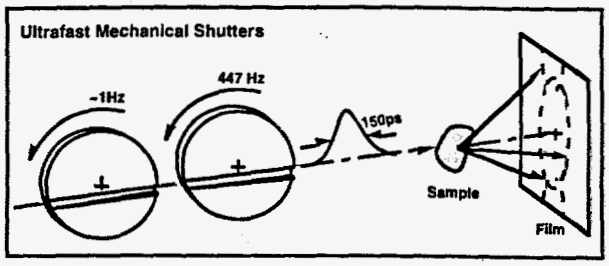

Fig. 2. Schematic view of rotating mechanical collimator system for selecting a single x-ray pulse from ~μsec spaced synchrotron x-ray pulses.

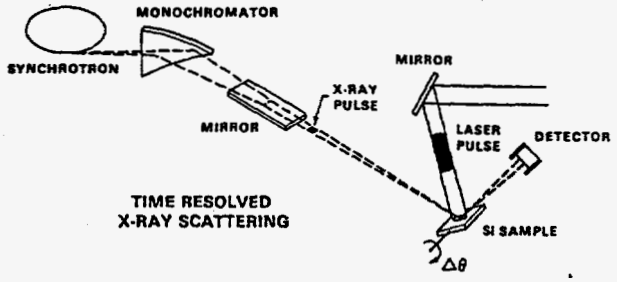

Fig. 3. Schematic view of a scintillation detector gated in coincidence with a laser pulse and a probing synchrotron x-ray pulse.

Nanosecond time-scale modulation of the high voltage on microchannel intensification plates can be used to make 2-dimensional single pulse measurements at synchrotrons if the low efficiency (~a few percent) of photocathodes can be tolerated. Unfortunately, ordinary x-ray phosphors have long lived tails that prevent their use in cases where the time of microseconds or shorter are needed.

In cases where spatially resolved detection is not required, it is quite feasible to use schemes as conceptually simple as electronic gating of scintillation detectors in connection with synchrotron and other x-ray time-structures. Larson[15,8] et al. used the pulse-height integration of simultaneous photons (i.e. from a single monochromatic synchrotron pulse) in a NaI scintillation detector to make quantitative photon counting measurements of Bragg diffraction profiles during pulsed laser melting of Si. This technique took advantage of perfect Si and Ge crystals, which provided arcsecond range angle resolved Bragg scattering (step-scanning mode) together with nanosecond temporal resolution synchronization of x-ray and excimer laser pulses as illustrated in Fig. 3.

X-ray streak cameras provide extremely high temporal resolution and are well adapted to pulsed time-structures from the standpoint of recycling and synchronization. Streak cameras have been used extensively in connection with soft x-ray detection, whereas their use with hard x-rays has been limited, partially because of the effciency of photocathodes, which are typically are only a few percent for hard x-rays. Tomov[17] et al have used a streak camera in connection with TTT measurements and Larsson[16] et al have shown the ability to measure the time structure of the ALS synchrotron pulses with ps resolution. Woolsey and Wark[18] and Whitlock and Wark[2] have also used streak cameras to time resolve the compression dynamics in single shot shock loading studies. Further development of streak camera techniques, such as a jitter-free technique suggested by Mourou[14] would have the potential to greatly improve the investigation of the fastest transient effects.

Pixel array detectors represent an important prospect for situations in which position sensitive, time-resolved x-ray diffraction measurements are needed. An initial design for a very high performance 2D array detector, with separate energy detection capability for each pixel and time-resolution in the 200 nanosecond range, was discussed a number of years ago,[19] but such a detector is not yet realizeable. The detector development effort initiated by the group of Gruner[20] has tested 4 × 4 pixel array prototypes of a detector with a burst mode that is capable of accumulating ~8 two-dimensional arrays of data with ~200 nanoseconds between measurements. Larger, 100 × 92 pixel arrays are under construction and testing[20] for radiation hardness as well as detection capability.

Progress on the development of detectors with higher temporal and spatial resolution, the inclusion of energy resolution, and radiation hardness will play a key role in the ongoing development of virtually all x-ray diffraction investigations. Time-resolved investigations in general, and pulsed-source time-resolved investigations in particular will require higher capability detectors in order to take advantage of both present and future pulsed x-ray sources.

4. APPLICATIONS OF PULSED TIME-STRUCTURE X-RAY BEAMS

4.1 Shock Loading Materials Response

As discussed above, Quinton Johnson et al initiated a series of nanosecond range time-resolved x-ray diffraction measurements beginning in 1967,[4,21] investigating the crystal structure and compression characteristics of materials as a function of explosive shock loading. They studied the lattice parameters of LiF, Al and graphite during the shock process induced by explosive detonations, using separate scintillators as well as film to capture the temporal changes in lattice parameter as a function of the compression and rarefaction characteristics of the shock phenomena. One of the important initial results of these measurements was that materials remained crystalline during the shock process.

Because of the inhomogeneous deformation of materials as they undergo shock loading and the high speed (μm/ns) with which

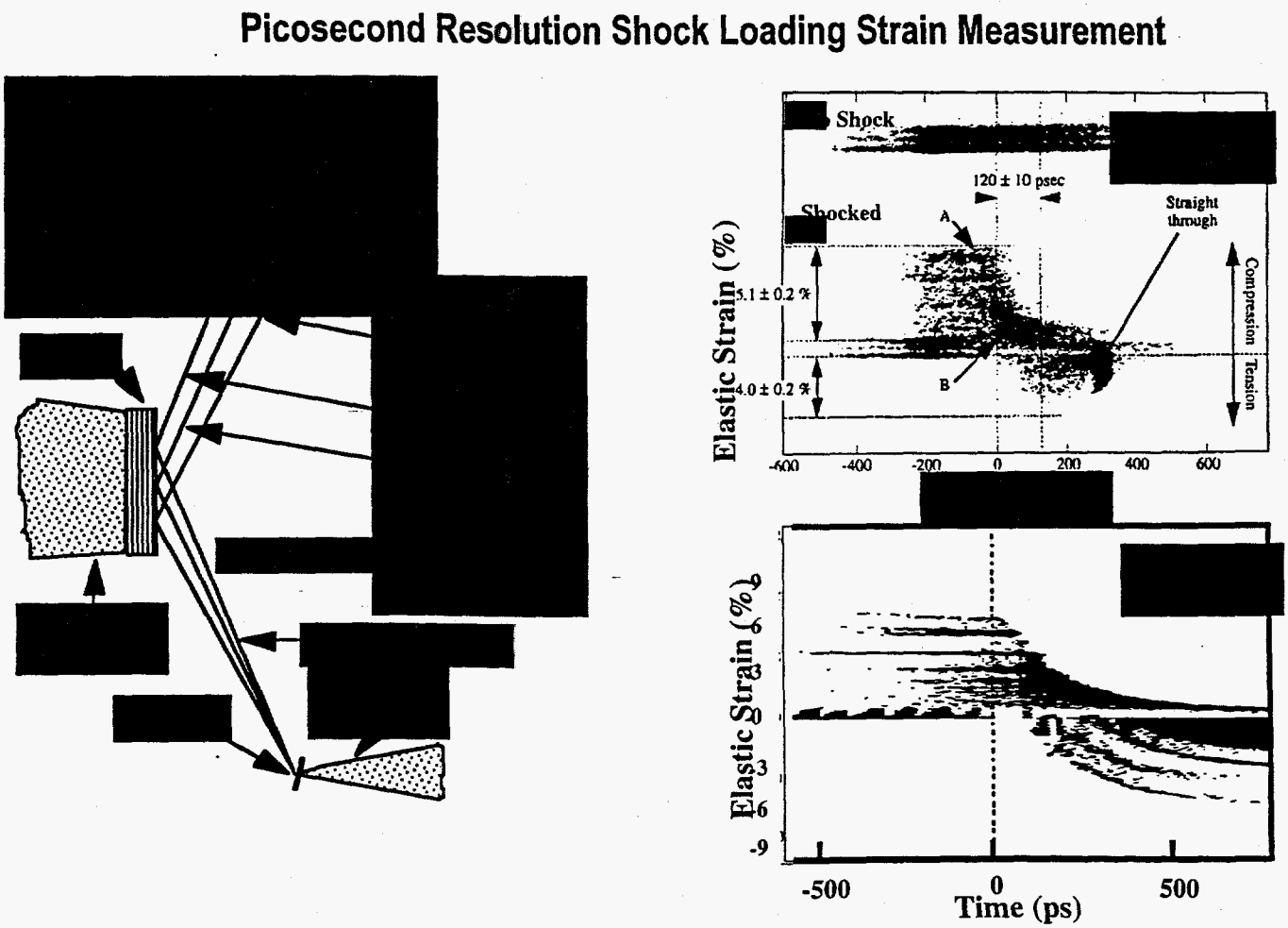

Fig. 4. Experimental configuration for picosecond range measurement of shock loading breakout using a pulsed-laser x-ray source and streak camera detection of compresion and tensile strain.

shock fronts propogate, investigations as undertaken by Johnson et al above, and more recently those of Whitlock and Wark,[2] andWoolsey and Wark[18] represent extremely complex measurements requiring careful attention to the entire process.

Figure 4 depicts a scattering geometry utilized by Wark[22] et al in which the compression wave is measured as it breaks out through the rear surface of the sample, and the penetration of the x-rays provides a tool to monitor the reflected wave as well. In their experiments, they typically utilized a laser-plasma x-ray generation and a laser-explosion induced shock wave so that it is possible to synchronize the shock and x-ray generation to ~100 ps. Detailed investigations of both the loading and unloading phase of shocked crystals have been performed using the geometry in Fig. 4 (left) in which the shock loading, the x-ray pulse, and the streak camera are all synchronized. Figure 4 (right) shows a streak camera recording of diffraction from a silicon 111 oreinted crystal as the shock wave emerges at the back side of the crystal; the lower panel shows a detailed simulation of the process using a version of the MEDUSA, one-dimensional Lagrangian hydrocode developed in the laser fusion program. These single shot measurements are well represented by the calculations. In particular, the large compressive and dilatational strains, which are considerably larger than the static fracture strain of ~2.5% for Si, should be noted. The time structure of the shock unloading as the dilatation changes from compression to tension provides information on the thickness of the shock front as well as the magnitude of the compressive wave that traversed the crystal and impacted the crystal surface.

4.2 Laser Melting in Semiconductors and Melt-Solid Interface Temperatures During Rapid Regrowth

Initial measurements utilizing the pulsed time-structure of synchrotrons for time-resolved diffraction[15] were studies of pulsed-laser melting, regrowth, and (liquid-solid) interfacial overheating and undercooling in Si and Ge. These measurements made use of the high angular resolution of synchrotron beams and performed measurements as a function of angular rotation of the sample to obtain near-surface thermal strain distributions through detailed fitting of numerical diffraction calculations to the time-resolved measurements. Nanosecond resolution measurements of the pulsed-laser induced Bragg peak modification were obtained in a step scanning mode using a simple gated NaI detector and synchronizing the arrival of laser pulses with the arrival of a probing x-ray packet. Analysis of the (thermal induced) strain scattering yielded temperature profiles and interface undercooling during the rapid (5 m/s) regrowth of Si following pulsed laser melting[8, 23].

The measured time-resolved temperature profiles were found to be in remarkably good agreement with detailed calculations for thermal heat flow. Making use of the x-ray time-resolved measurments of the interface temperature at the (zero-velocity) maximum melt depth penetration, the extent of undercooling at the interface for velocities varying from 0-to-5 m/s during regrowth was obtained. As indicated in Fig. 5 undercooling of approximately 11 K/m/s was found for regrowth in the <111> direction, while only half that amount of undercooling (5.6 K/m/s) was found for regrowth on <100> oriented Si.[23] Although the principle of micro-reversibility would imply symmetry between melting and regrowth, we

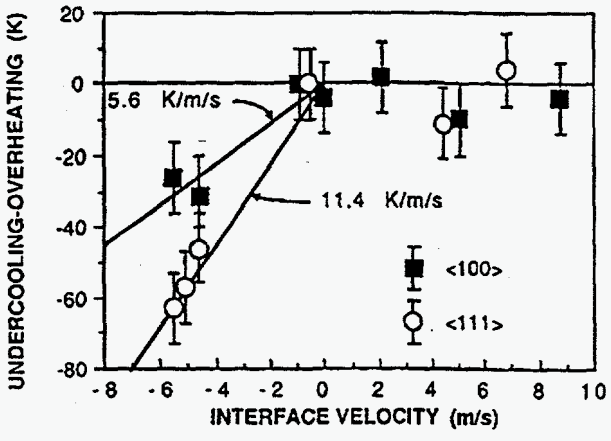

Fig.5. Liquid-solid interface temperature in Si during rapid laser melting (Pos.) and regrowth (neg.) determined using nanosecond resolution time-resolved x-ray diffraction.

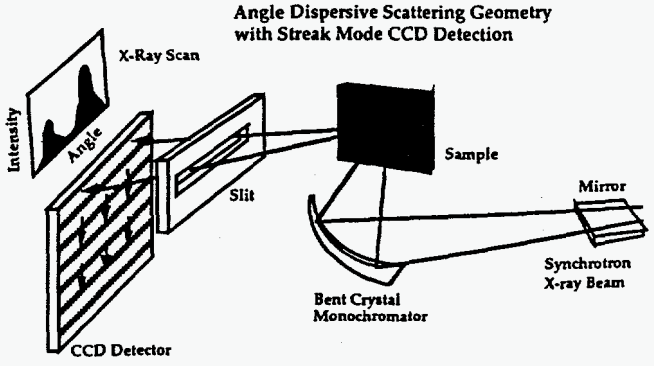

Fig. 6. Schematic view of a streak-mode CCD x-ray detector in combination with a focusing Lemonnier geometry monochromator, providing for simultaneous measurement for a range of angles along a radial diffraction direciton.

note that (within the estimated uncertainties) no significant overheating was observed during melting even though melting was nearly twice as fast as regrowth. Interface morphology differences such as faceting during could produce an asymmetry.

The high brilliance of the ESRF, the APS, and SPRing-8 and the addition of time-slice 2D detectors will make possible studies of rapid thermal transport, rapid transport Kapitza thermal resistance at heterointerfaces, and even structural investigations of overheated and undercooled liquid layers on crystal surfaces feasible. Such measurements of thermally induced effects have not been pursued as of yet. Since the transfer of laser energy (absorbed by electrons) into phonons occurs on a time scale of tens of picoseconds, streak camera detection techniques that have been developed will now make superheating (i.e before melting is nucleated) and the melt nucleation process during picosecond laser pulses possible.

If additional developments in the speed of 2D CCD x-ray detectors can be made, the Lemonnier focusing[24] geometry as used by Clarke and Lowe during rapid thermal processing of Si-Ge strained layers[25, 26] could be applied in connection with individual synchrotron radiation pulses. CCD detectors operating in the streak camera mode (as shown in Fig. 6) would significantly impact the direction of investigations of laser melting discussed above. That is, a Lemonnier monochromator used in connection with a CCD recording an entire diffraction scan would result in ~150 ps resolution for the entire scan without repeated measurements at each angle.

4.3 Laser Heating Using Table-Top Terawatt (TTT) Lasers and X-Ray Diode Sources

Tomov[17] et al and Chen[27] et al have discussed the development of pulsed x-ray generation and both picosecond and nanosecond diffraction investigations of transient heating using a TTT laser driven x-ray diode pulsed x-ray source. Unlike the single shot experiments associated with shock loading studies above, these experiments represent reversible conditions conducted using thousands of repeated cycles, recording the results on film or CCD x-ray detectors. The multiple-shot mode of measurement relies on uniform amplitude laser pulses and the recycleability of the sample as well as the phenomena under study in addition to precision timing. Studies of picosecond and nanosecond range laser-heating in Au and Pt have been reported using an overall configuration similar to that shown in Fig. 7. Time resolution as low as 10 ps has been achieved so far, and the investigations of laser-heating of metals have been compared with one-dimensional heat flow simulations. Preliminary measurements have been made indicating that the inter- and intra-molecular structural dynamics of liquids may be possible using this technique. The fact that these measurements are made in a home laboratory, rather than, say, at off-site synchrotrons or at large pulsed laser facilities, is important in establishing a more general application of such types of study. In particular, when combined with expectations of higher power shorter pulse-length lasers,[14] the outlook for further development and application of these and additional time-resolved methods is good.

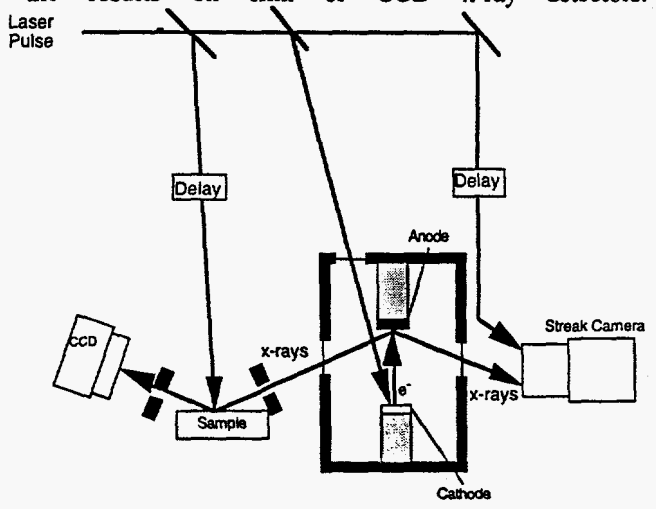

Fig. 7. Typical geometry for a pulsed-laser pump-probe time-resolved x-ray diffraction mesurement using an x-ray diode source, streak-camera timing, and CCD detector.

4.4 Pulsed-Laser Deposition Thin-Film Growth and Surface Kinetics

The non-equilibrium synthesis of thin-film materials and multilayer structures is unrivaled as a source of new materials for advanced technologies, including deposition and layered growth of semiconductors, metals, complex high-temperature superconductor oxides, compound semiconductors, and a host of other materials. Fig. 8 contrasts pulsed-laser deposition (PLD) as a thin-film growth process with continuous processes such as molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). Pulsed growth separates the deposition and aggregation phases so that they can be investigated individually, while deposition and growth are continuous and concurrent for MBE and CVD. Therefore, real-time x-ray measurements performed during the deposition and aggregation phases have a unique opportunity to investigate the fundamental aspects of both the deposition and aggregation processes. Only archeology-like inferences can be made on the growth processes from static measurements of the completed film at the bottom of the left panel. In situ time-resolved

measurements of PLD growth have been initiated at Oak Ridge National Laboratory using a high brilliance UNI-CAT undulator beam line at the Advanced Photon Source (APS). Although most aspects of film growth are on much longer time scales than the pulsed time-structure of synchrotrons, the initial energetic laser ablated species arrive within microseconds and the impact of these high energy particles on the surface structure is at present unknown. In favorable cases, it will be possible to observe the surface dynamics of deposition and growth with microsecond resolution using single x-ray pulses.

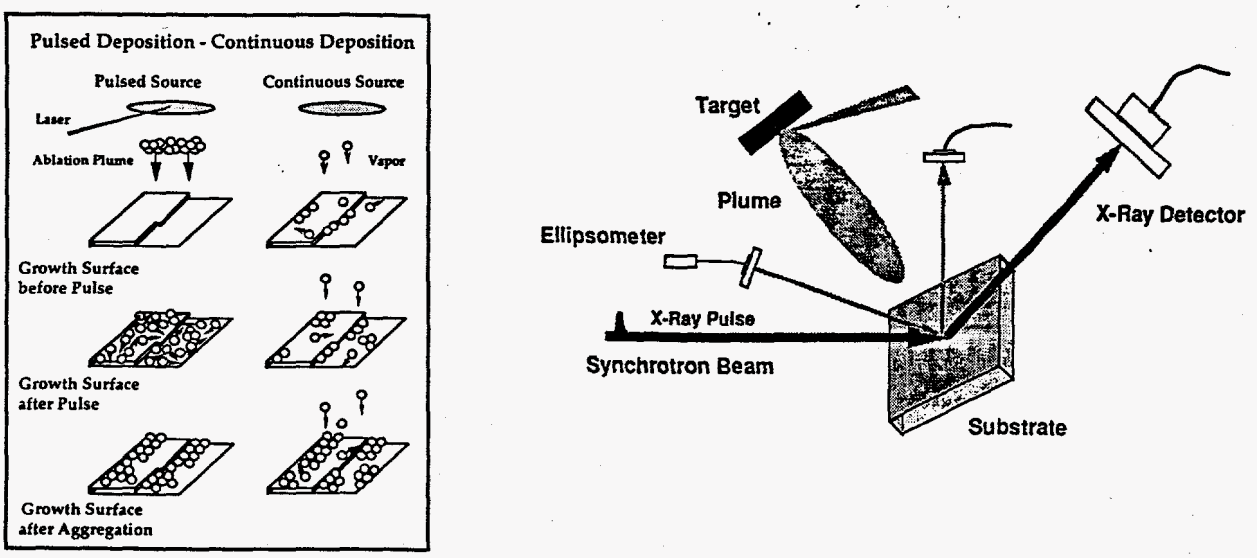

Fig. 8. Schematic comparison (left) of pulsed-laser deposition conditions with continuous CVD or MBE growth conditions, and the scattering geometry for time-resolved surface x-ray diffraction measurements of non-equilibrium growth.

On a much finer temporal resolution scale involving a multilayer material, Rishel[9] et al have demonstrated the use of 130 femtosecond 7.5 Å x-ray pulses to monitor laser heating induced disorder, thermal expansion, and vaporization of cadmium arachidate (fatty-acid) Langmuir-Blodgett multilayers. Laser pulses of 130 fs duration were split from the heating laser pulse and used to generate the 130 fs 7.5 Å wavelength Si K_α x-ray pulses, which were then monochromated and focused onto the sample as it was being heated by the remaining portion of the 130 fs laser pulse. The angular width of the focused x-ray pulses served to angularly disperse the Bragg reflection accross a CCD detector, making it possible to determine the time evolution and disappearance of the entire Bragg peak. Each 130 fs x-ray pulse contained ~5×10^4 photons angularly dispersed over 1.5 degrees. Observation of atomic disorder (non-thermal bond breakdown) was deduced by the loss of structural Bragg scattering on a 650 fs time scale, a significantly long time before the transfier of electronic energy could be tranfered into the nuclear motions in the form of phonons. These experiments, some of which are discussed elsewhere in this symposium by the authors, represent exciting regimes for x-ray investigation of photo-induced chemical and electronic effects. This area is, of course, of active theoretical interest in analyzing both the optical and x-ray pump-probe experiments on bond dynamics[28]

The study of biological processes by infrared, visible, and violet optical wavelength probes has been made possible by the availability of ultrafast lasers, and much information has been obtained regarding the electronic dynamics of molecular systems. Although related to the present section more by process than sample, Ráksi[29] et al have investigated the photodissociation of gaseous SF_6 with 1.5 ps time-resolution through the use of x-ray near-edge absorption shape resonance structure,[29] using laser generated x-ray pulses to study laser induced molecular dissociation. Absorption methods involving chemical bonding and reactions are likely to prove to be quite attractive because of the relatively simple measurement geometry and the homogenous and regenerative nature of liquid and gaseous materials compared to crystals.

4.5 Structural Dynamics of Biological Materials

The basic chemical processes of biological materials takes place in the form of enzyme-catalyzed reactions. Gai[30] et al point out that these reactions are remarkably efficient and selective, and in many cases are strongly impacted by the architecture of the protein solvent. Since the structure of proteins provides sites for storing intermediates and creates species selective passage between the active sites and the surrounding solution, it is necessary to understand the impact of the protein structure

on chemical dynamics in order to understand and predict the complex chemical behaviour within the protein. Nanosecond resolution investigations of biological materials was first demonstrated by Moffat using single pulses of white beam synchrotron radiation in measurements at the Cornell High Energy Synchrotron Source (CHESS) as reported by LeGrande[13] et al. This technique, using a rapidly rotating slit in series with either a more slowly rotating slit or an electromagnetic blade, mechanically ensures that only single synchrotron x-ray pulse exposures of Laue diffraction patterns are collected on film or CCD detectors.

By directing optical laser pulses on the sample in coincidence with the synchroron x-ray pulses, it has been possible to investigate[31] the kinetics of photolysis in carbonmonoxy myoglobin, MbCO. Using the ID-9 white beam line at the European Radiation Synchroron Facility (ESRF) and initiating photolysis with 7.5 ns laser pulses, Srajer[31] et al monitored crystallographically heme and protein relaxation in MbCO as CO was was photodissociated and allowed to rebind. Although discussion of crystal structure of MbCO is beyond the scope of this paper, it was found that the magnitude of the x-ray structural changes as a function of time could be correlated with optical spectroscopy and molecular dynamics models; thus demonstrating the ability to perform nanosecond resolution crystallographic dynamics.

More recently Perman[32] et al reported time resolved x-ray investigations of structural changes in photoactive yellow protein (PYP) (an axanthopsin bacterial photoreceptor) during light absorption, again using the ID-9 white beam line at the ESRF and a 7 ns laser to initiate the photocycle. They were able to determine the structure formed within one nanosecond after the photo-excitation, but that higher resolution than the 7 ns laser pulse will be needed to time-resolve the actual development of this structure following absorption of light. Other more slowly forming states in the photon transduction process were followed within the time-resolution of the experiment and associated with structural changes. We note that, as in the MbCO study above, investigations of the structural dynamics associated with basic biological processes such as photosynthesis and photodissociation require single pulse sources, and that as is well known from optical spectroscopy studies, structural investigations with time-resolution significantly faster than nanoseconds are required. Nevertheless, results such as these clearly indicate the power of x-ray crystallography as an additional tool in the investigation of complex biological processes.

4.6 Nuclear Resonant Synchrotron Scattering Investigations

A new and very active area of x-ray scattering relying completely on the pulsed time structure of synchrotron sources is the use of time-domain Mössbauer nuclear resonant scattering and absorption spectroscopy for the investigation of the dynamics and magnetic properties of materials. The typically ~100 ns or greater spacing of synchrotron pulses is almost perfectly adapted to the 141 ns decay time of the ^{57}Fe 14.4 keV resonant (excitonic) state. In general, these studies are built around the nanovolt-range energy selection associated with the excitation of Mössbauer nuclei and the (141 ns decay rate) time-domain separation of the resonant photons from the prompt (meV - eV bandwidth) photons. That is, resonant excitations in a resonant foil (or resonant Bragg monochromator) and scattered in the forward (or Bragg) direction, respectively, provide a number of options for designing quasi-elastic or high resolution inelastic scattering investigations.

Figure 9 shows the delayed time-spectrum[33] of Mössbauer resonant photons from an electronically forbidden (777) reflection of an antiferromagnetic $^{57}Fe_2O_3$ monochromator. The decay rate and the hyperfine oscillations are in good agreement with theory.

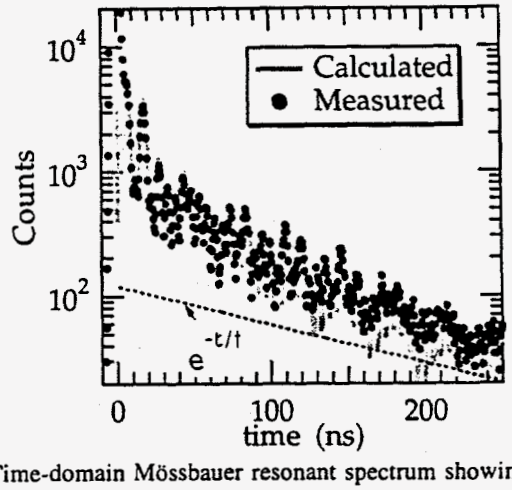

Fig. 9. Time-domain Mössbauer resonant spectrum showing the decay and the beating between the split energy levels.

Using the 150 ps synchrotron pulselwngth to separate the neV resolution-range resonant photons from the ~eV resolution prompt electronically scattered photons, synchrotron resonant excitation has been well studied[34] so that these phenomena can be applied to fundamental investigations of condensed matter physics.

For example, the pulsed time-structure of synchrotrons together with nested and/or highly asymmetric meV range monochromators provide milli-electronvolt resolution phonon density of state (DOS) measurements on materials containing Mössbauer nuclei. Seta[35] et al and Sturhahn[36] et al have applied incoherent Mössbauer excitation of ^{57}Fe in a-iron and ^{57}Fe enriched stainless steel to measure the phonon DOS associated with Fe. In these experiments, the ~a few meV resolution synchrotron x-ray beam was scanned over a range of ± 40 meV range near the 14.413 keV ^{57}Fe Mössbauer energy; these investigations used phonon-assisted incoherent Mössbauer absorption as measured through time-delayed monitoring of 14.4 keV emission and delayed Fe fluorescence using a configuration similar to that in Fig. 10.. Since incident photons with energies of say 10 millivolts off the Mössbauer resonance can excite an ^{57}Fe nucleus only with the aid of a 10 meV phonon upscattering, the incoherent decay channel as a function of the incoming beam energy provides a measure of the density of 10 meV phonons. This novel application of synchrotron excitiation of Mössbauer resonant nuclei has been refined to the point that it now provides a method that is relatively fast and can be used on very small and polycrystalline samples; hence it is complementary to neutron techniques. Predictions that this technique would be useful for observing subtle lattice dynamics changes due to alloying, phase changes, have in fact materialized as will be discussed elsewhere in this volume.

Toellner[38] et al have reported sub-meV resolution nonresonant x-ray beams, which result in sub-meV resolution phonon DOS measurements such as are shown in the right panel of fig. 10, which are in excellent agreement with nwutron scattering measurements. In other experiments, DOS measurements have been made as a function of disorder and long-range order in alloys, and measurements have been reported on iron nanocrystals. To some extent this technique is limited by the requirement of Mössbauer resonant atoms, at the same time this very property also provides the potential for tagging specie specific phonon DOS effects in materials that either contain or can be doped with Mössbauer resonant nuclei. Yu. V. Shvyd'ko[39] et al have reported magnetic small angle scattering results for ^{57}Fe enriched iron, suggesting the further possibility of utilizing the brightness of 3rd generation sources to investigate magnetic domains under conditions such as high pressure, critical magnetic fluctuations, amorphous or polycrystalline magnetic materials.

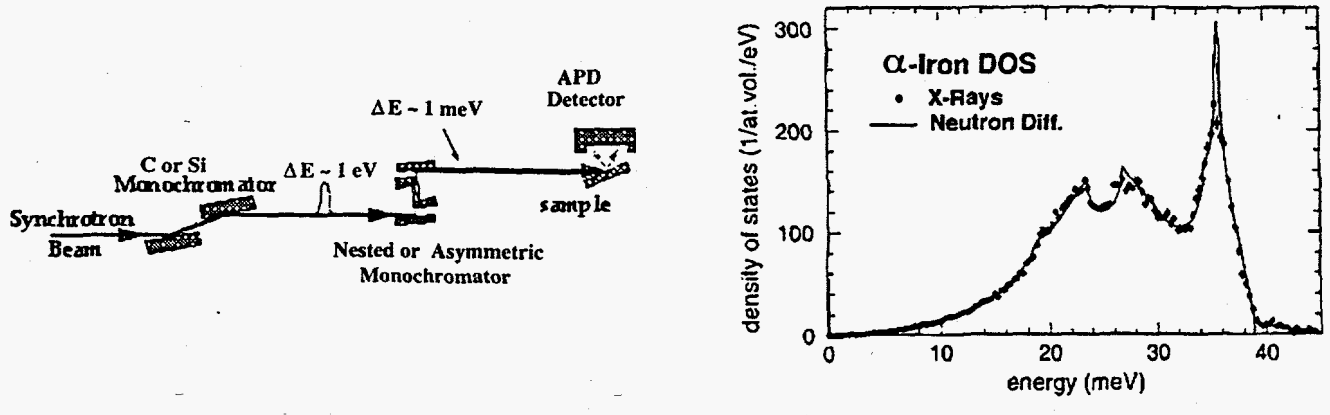

Fig. 10. Schematic view of the scattering configuration for meV resolution time-domain resonant spectroscopy (left) and the phonon density of states (right) measured for iron with ~1 meV resolution using a similar configuration (Ref. 31)

Using a synchrotron Mössbauer measurement technique not requiring resonant nucleii in the sample, Baron[40] et al have investigted structural relaxations in glycerol. As shown in Fig. 11, the use of a ^{57}Fe foil before the sample and an identical, but slightly Doppler shifted detector foil after the sample makes it possible to detect quasielastic scattering in the sample. The sensitivity is through the time-domain measurement of the disruption of the beating between the Doppler shifted absorbers (i.e quasielastic line broadening of the energy width of the beam striking the second absorber). Such measurements are complementary to present x-ray correlation spectroscopy time scales of ~1 ms, and are an alternative to neutron scattering investigations for large wave vectors and high energy resolution.

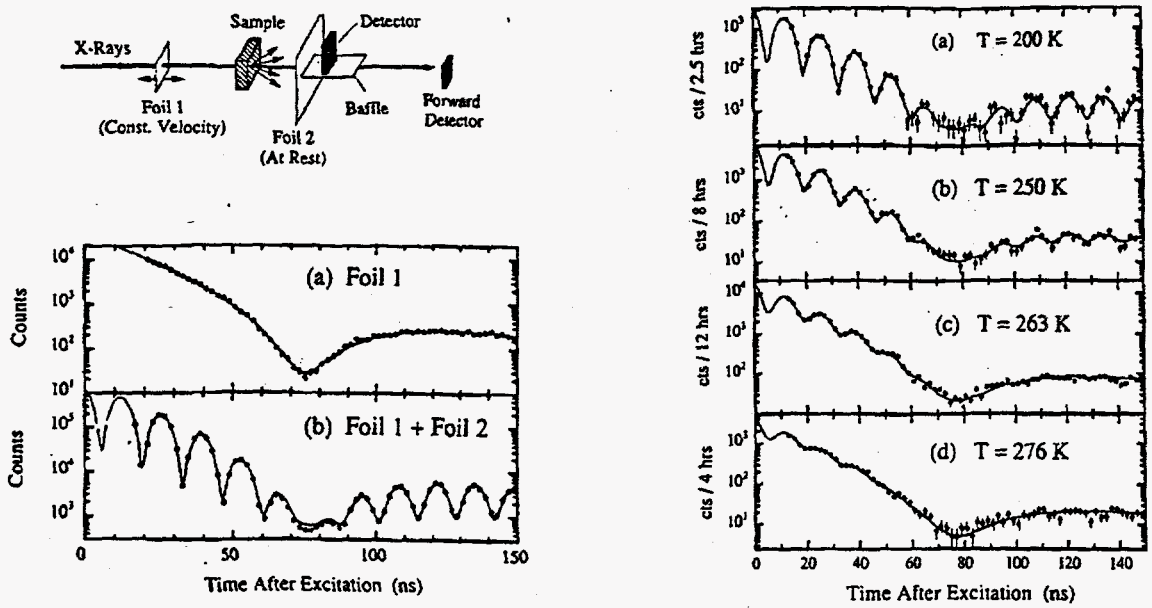

Fig. 11. Time-domain Mössbauer resonant spectroscopy configuration for investigating quasi-elastic scattering in non-resonant materials (upper left). The lower left panel shows the beat pattern for a constant Doppler shift of foil 1, and the right panel shows the effect of temperature dependent quasielastic scattering of the sample on the beat pattern, (Ref. 40).

A related development that has been pursued for some time is a Doppler tuneable (~meV) Mössbauer resonant spectroscopy using reflection from a rapidly spinning (in-plane) resonant thin-film yielding μeV resolution. As reported by Röhlsberger[37] et al, such widely Doppler-tuneable devices are expected to be useful in investigating soft modes, rotational excitations, and the fundamental aspects of diffusion.

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