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Final Report

"Operation of Beam Line Facilities for Real-time X-ray Studies at Sector 7 of the Advanced Photon Source"

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DOE Patent Clearance Granted
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SUMMARY

This Final Report documents the research accomplishments achieved in the first phase of operations of a new Advanced Photon Source beam line (7-ID MHATT-CAT) dedicated to real-time x-ray studies. The period covered by this report covers the establishment of a world-class facility for time-dependent x-ray studies of materials. During this period many new and innovative research programs were initiated at Sector 7 with support of this grant, most notably using a combination of ultrafast lasers and pulsed synchrotron radiation. This work initiated a new frontier of materials research: namely, the study of the dynamics of materials under extreme conditions of high intensity impulsive laser irradiation.

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1. Overview of Research Mission at Sector 7, Advanced Photon Source

MHATT-CAT (Collaborative Access Team) is a consortium formed between a large publicly-funded university (Michigan), a major Ph.D.-granting HBCU institution (Howard University), and a prominent industrial research laboratory (Bell Labs), with strong collaborative ties to several National Laboratories. MHATT-CAT is therefore uniquely positioned to provide extensive training experiences for undergraduates, graduate students, and postdocs, as well as educational enrichment experiences for pre-college students. In particular, MHATT-CAT has been successful in translating the excitement generated by the science it performs into a wider involvement of synchrotron users from groups that are traditionally under-represented at national science facilities. Continuing to build a more diverse base of users is central to our research mission.

MHATT-CAT's scientific program centers on real-time x-ray studies of materials and exploits the unique characteristics of the APS source. This research theme is made possible by the unprecedented brilliance of undulator radiation at the Advanced Photon Source, opening the door to new capabilities that were not previously possible:

- studies of materials and devices under actual operating conditions
- exploiting the microfocus capabilities of high-brightness x-ray beams
- using ultrafast lasers to coherently control states of matter and dynamics [1,2]*
- probing the microscopic behavior of interfaces and buried layers
- investigating length-scale dependent ordering and relaxation processes in real-time
- studying the dynamics of 'soft' condensed matter, including polymers, complex fluids, and biological materials.

An important aspect of MHATT-CAT's research program is the development of new techniques for studying the dynamics of materials. For example, under the current grant, we have taken the lead in developing a microdiffraction facility combining novel focused x-ray techniques with in-situ scanning probe microscopy. In another area of materials dynamics, X-ray Photon Correlation Spectroscopy (XPCS) takes advantage of the high degree of transverse coherence of undulator beams, permitting studies of the internal diffusion and relaxation of materials. The work funded under this grant contributed in important ways to the development of these new fields and they are an important ongoing component of the CAT's science program at the APS. A further area in which the CAT has notable strengths is in the use of ultrafast optics and detectors. Both Howard and Michigan have active programs in ultrafast optical science, so this direction is expected to play an important role in the development of the CAT's science program over the next several years. Recent accomplishments supported by this grant are highlighted in Section 2.

*Note: References in square brackets refer to refereed publications of work supported by this grant (see Section 3).

2. Progress and Accomplishments under U.S. Department of Energy Award No. DE-FG02-99ER45743, November 1, 1998 – December 31, 2002.

This section describes the scientific accomplishments that have been achieved at Sector 7 with support from this award during the first four years of its operation. We have pursued a vigorous scientific program and have achieved leadership in a number of important areas. In particular, research carried out at Sector 7 facilities has opened up the new field of x-ray microbeam studies of materials. This work first demonstrated the use of pre-figured elliptical K-B mirrors to achieve sub-micron spot sizes. [3] This development was recognized by an "R&D 100" Award in 2000. Many studies have been carried out at Sector 7 using this novel approach; for example, to study strain in microchip interconnects, and most recently to probe the stress field around a nano-indentation tip. A second important area pioneered with support from this grant is picosecond diffraction using ultrafast laser pump-probe techniques. These experiments led to the first ultrafast Bragg-switch, a new way to produce femtosecond scale x-ray pulses [1]. An extensive research program utilizing these new capabilities is now underway at the dedicated end-station 7-ID-D. We reported exciting results on this topic in Physical Review Letters, demonstrating the coherent control of phonon strain fields in semiconductors. [2]

A wide range of experiments exploiting the special characteristics the APS have been successfully performed at Sector 7 over the course of this award, many of which are in the "first of a kind" category. Some highlights include:

- First *in-situ* measurements of stress-induced phase transitions in nano-indented semiconductors
- First demonstration of spatially-resolved crystallographic texture mapping of high-T_c superconducting tapes
- Studies of dynamics of binary liquids and polymers using x-ray photon correlation spectroscopy
- Studies of giant magnetoresistance materials using high pressure near-edge x-ray spectroscopy
- First demonstration of two-beam coherent truncation rod diffraction for direct determination of interfacial atom arrangements in electronic heterostructures
- Microfocus studies of fiber optic components using Bragg-Fresnel optics
- Real-time x-ray studies of annealing
- Time-resolved studies of non-thermal melting and surface structure dynamics using ultrafast x-ray pump-probe techniques
- First three-dimensional tomographic maps of concrete aggregates identifying phases associated with weathering and deterioration

The grant to MHATT-CAT has enabled collaboration with over 50 scientists from 16 different institutions, including 4 national labs, 9 universities, two of which are HBCU institutions, and several corporate labs. 15 refereed journal articles, and a further 16 refereed conference proceedings articles, have so far resulted from these collaborations.

A major goal of MHATT-CAT is attract a broadened, and more diverse, pool of users to the Advanced Photon Source. As a consortium represented by collaborations between major academic, industrial and government research institutions, MHATT-CAT is well placed to provide training and educational enrichment experiences at the frontiers of synchrotron radiation research. In this context we note that an increasing number (> 40) of graduate and undergraduate students and postdocs have benefited from their involvement in research supported by this award.

In the following section we highlight some of the scientific accomplishments of this grant, illustrating our progress with examples of a few selected projects drawn from the approximately 60 experiments that have been performed at Sector 7 over the curse of this grant. These examples are representative of the exciting forefront studies that are becoming the hallmark of the APS.

Research Accomplishments: Selected Examples -MHATT-CAT has made notable contributions to several new frontiers of x-ray science, including: microbeam research, ultrafast x-ray diffraction, photon correlation spectroscopy, and coherent beam diffraction. Here we give examples of our accomplishments in each of these areas.

2.1 Ultrafast Pump-probe Diffraction Measurements using Femtosecond Lasers

(D. Reis, P. Bucksbaum, R. Clarke, R. Merlin, University of Michigan)

The high brilliance of synchrotron radiation provided by 3rd generation synchrotrons such as the APS enables pump-probe diffraction experiments on thin films and nanostructures. MHATT-CAT scientists have initiated new ideas for ultrafast x-ray difrraction using coherent control of impulsively generated phonons. In this innovative approach, crystal momentum transfer from a superlattice created by coherent phonons is used to operate a "Bragg Switch" for the production of sub-picosecond x-ray pulses. We have recently demonstrated [1] the feasibility of this approach at the femtosecond laser facility we have built at 7-ID-D. We were able to observe the propagation dynamics of the strain field associated with coherent phonons.

Using the ultrafast diffraction capability at 7ID-D we have demonstrated the feasibility of performing picosecond diffraction measurements and have carried out a number of pump-probe experiments on semiconductor crystals such as indium antimonide. Fig. 1 shows the time-resolved x-ray scattering from InSb that we recently reported in PRL [2].

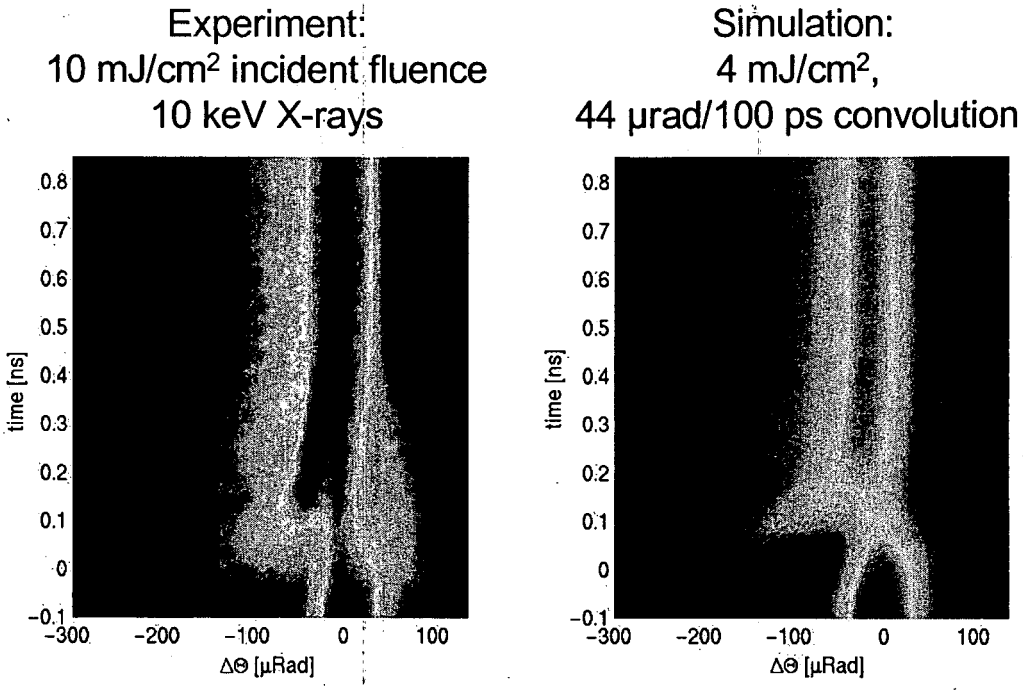

Fig. 1: Time-resolved x-ray diffraction at MHATT-CAT's 7-ID beamline. The deflection towards smaller angles seen immediately after the laser pulse is caused by a transient expansion of the lattice due to the passage of a coherent acoustic phonon. The return to thermal equilibrium is slow on this time scale.

The importance of these measurements is that we have shown it is possible to coherently control the dynamics of atomic lattices on picosecond time scales. This opens up a new area of solid state physics and chemical studies that was previously inaccessible. We envision many new applications including excited state structural measurements, coherent control of chemical reactions, real-time studies of electronic excitations, and real time studies of systems exhibiting soft modes, such as ferroelectric materials.

2.2 X-ray Microbeam Studies

The vision of MHATT-CAT Associate Director, Walter Lowe, to devote a significant portion of the Sector's initial operation to microbeam studies, has paid off well. In collaboration with scientists at Oak Ridge National Lab (Gene Ice, Ben Larson, John Budai, Jon Tischler and others) MHATT-CAT has established a strong presence in x-ray microprobe studies during the period of this grant. Over a dozen papers, and many invited talks and presentations have resulted from this collaboration.

2.2.1 In-situ Strain Mapping in Nano-indentation

W.P Lowe, Howard University, **David Schaefer, David Domzalski and Jason Martin**, Towson University; **Dohn Arms**, XFD/APS.

There is a strong need for an integrated tool that can study surface and interior features of materials simultaneously. The obvious choice to fulfill these requirements is to integrate a Scanning Probe Microscope (SPM) with a deep probe such as x-rays. Advancement in SPM technology has resulted in instruments that operate in many different modes at extreme surface resolution. Furthermore SPMs do not place stringent requirements on sample preparation and they are commercially available in many variations. In the present arrangement (Fig. 2) a nano- indenter has been set up on our undulator beam line along with the SPM. Using the nanoindentor it is possible to measure mechanical properties as well as *nano-fabricate* special test structures.

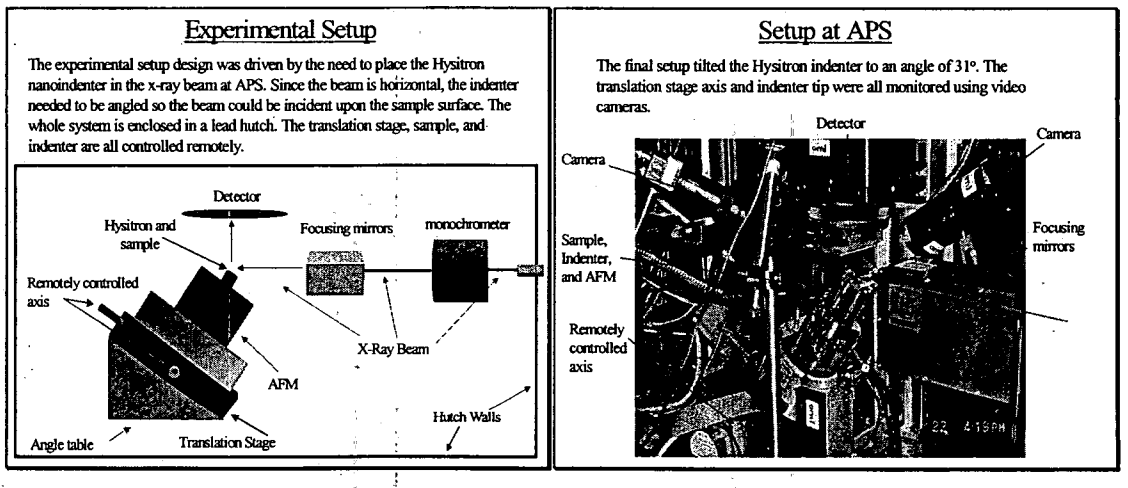

Fig. 2: AFM-Nanoindenter-Microprobe Set-up at MHATT-CAT's 7-ID-B Beamline.

Our initial studies were on Si monocrystals. Previous high-pressure studies of Si and Ge monocrystals show several structural transformations. Using the nanoindenter and the x-ray microbeam, the structural transformations can be studied directly. Fig. 3 illustrates the changes in microdiffraction that occur in the vicinity of the nano-indentation tip during one of these structural transitions.

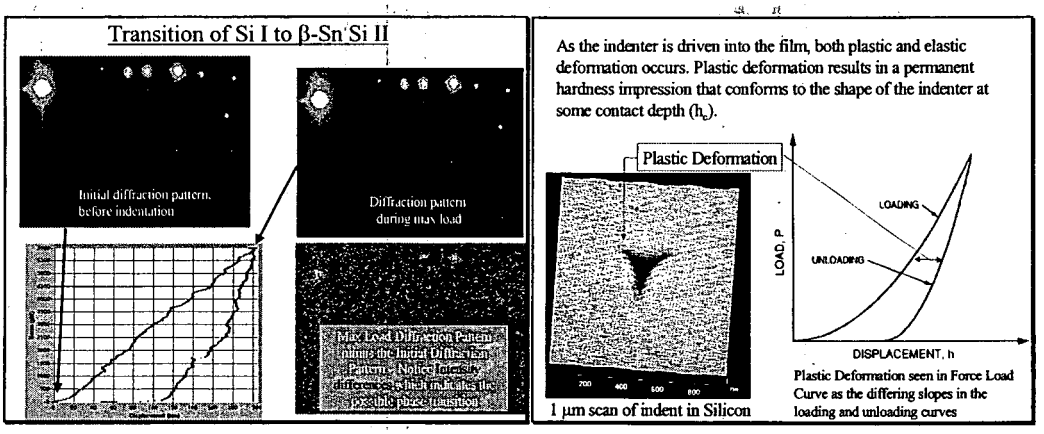

Fig.3: Nano-indentation induced transformation of Si studied by microdiffraction. The panel in the lower left shown the stress-strain data during loading and unloading. The panel on the far right shows an AFM image of the indented region where the microdiffraction was performed.

2.2.2. In-situ Microbeam Diffraction Mapping of Delayed Ettringite Formation In Concrete.

R.A. Livingston[1], R. Clarke[2], E. Dufresne, W. Lowe[3], E.O. Williams, Jr[4]

[1]Federal Highway Administration, McLean VA 22101, USA;
[2]University of Michigan, Ann Arbor
[3]Howard University, Beltsville, MD
[4]Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

A potentially significant cause of concrete deterioration is cracking associated with the presence of the calcium aluminate sulfate mineral, ettringite [$3CaO_X Al_2O_X 3CaSO_{4X} 32H_2O$]. This phase starts to form a few years after the concrete is cast. The specific mechanism causing its delayed formation remains controversial. To develop a better understanding of this process, the Turner-Fairbanks Highway Research Center of the Federal Highway Administration in collaboration with Howard University and the University of Michigan has performed a series of experiments in the laboratory on concrete specimens under controlled conditions. The primary damage data are obtained using a standard expansion measurement method (ASTM C490-86) at specific time intervals. In order to correlate this damage with delayed ettringite formation, it is necessary to have time-resolved data on the mineralogy of the specimen. However, conventional methods (SEM-EDAX, powder diffraction XRD or thermal analysis) require destructive sampling of the specimen. Also, these methods use very small sample sizes ~ 1 mg, which may not be representative of the heterogeneous concrete specimen. Energy dispersive diffraction using a synchrotron radiation source offers the possibility of a nondestructive method that can scan the mineralogy of a significant volume of concrete.

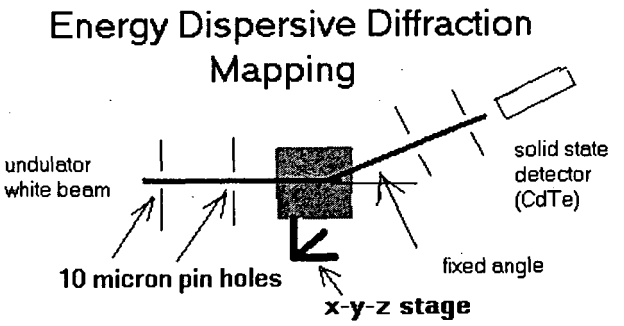

Fig. 4: High-energy microbeam diffraction set-up at 7-ID-B.

The specimen consisted of a 2 cm x 8 cm x 8 cm slab sawn from a concrete prism that had shown expansion on the order of 1% after 200 days. A white light beam (20<E<120 keV) was used to illuminate the specimen. The experimental set-up at MHATT-CAT's 7-ID-B enclosure is shown in Fig. 4. The energy dispersive diffraction spectra were taken in transmission mode using an Amptek CZT detector mounted at a 2θ of 10°. Typical voxel size was on the order of 1 mm^3. A rectangular region 20 mm x 5 mm x 2 mm through the specimen was scanned at a rate of 1 voxel per 10 seconds.

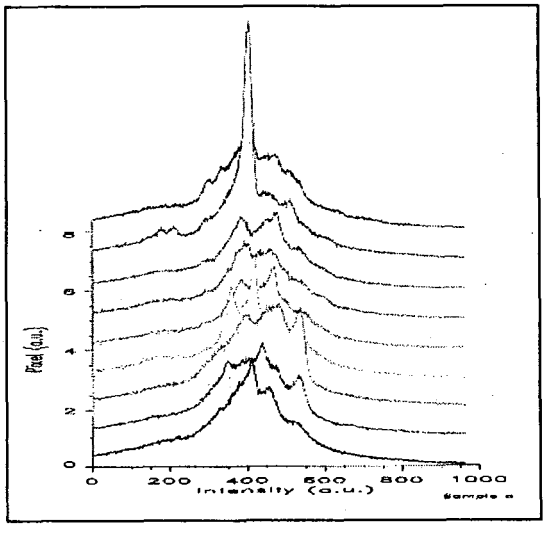

Fig. 5: Representative energy dispersive spectra of Ettringite phases in deteriorating concrete samples.

A total of 252 spectra were obtained over a period of 6 hours. Fig. 5 shows a series of spectra arranged in a stacked sequence corresponding to 8 different voxels of the sample. The variation from spectrum to spectrum is indicative of the spatially resolved distribution of mineral phases in the aggregate sample. Each peak in the spectrum is associated with a particular crystallographic d-spacing from one of these phases. In the next phase of this work we will "window" each of these energy dispersive features to construct a three-dimensional map of the mineral structure of the concrete samples, and in this way we will be able to study, in-situ, the spatial distribution of the phases such as

ettringite that are thought to be responsible for the failure of concrete. This is the first time that such maps have been shown to be feasible. Access to extremely intense high-energy (~100keV) x-rays at the APS is key to this technique.

2.3. Photon Correlation Spectroscopy

Studies of Dynamic Critical Behavior of Polymer Mixtures Using X-Ray Photon Correlation Spectroscopy. **Teamour Nurushev, Eric Dufresne, Roy Clarke, Steven Dierker**, Department of Physics, University of Michigan.

X-ray Photon Correlation Spectroscopy (XPCS) is an extension of the well-known and widely used Photon Correlation Spectroscopy (PCS), sometimes also called Intensity Fluctuation Spectroscopy. Probing the matter with coherent x-rays, instead of coherent visible light, makes it possible to probe the dynamic properties in a region of relaxation times (1 μs – 1000 s), and wavevectors q (0.004 – 2 Å $^{-1}$) that are inaccessible to visible light. XPCS capabilities were tested at this beam line with studies of the critical concentration fluctuations in the binary fluid mixture of Hexane-Nitrobenzene [4].

Recently we conducted studies of the dynamic critical behavior of binary polymer mixtures of Polystyrene/Polybutadiene using XPCS. Static and dynamic properties at the critical composition were measured. Effects of the damage to the sample caused by synchrotron radiation were extensively studied. The damage caused by radiation affects the scattering as well as relaxation time of the sample.

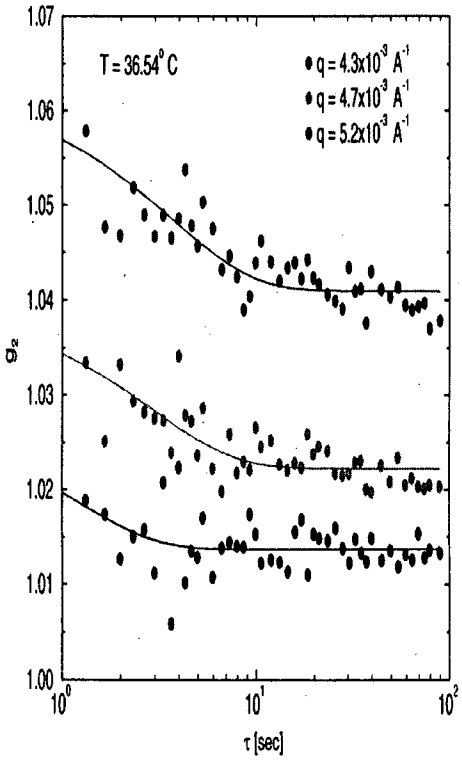

Fig.6: Correlation functions for 0.557 PS/PB ratio at T = 36.54.

The studies were conducted at the small-angle scattering facility in enclosure 7-ID-C. Because polybutadiene proved to be quite susceptible to x-ray radiation damage, it was necessary to use a monochromatic, rather than a pink, beam for the x-ray measurements of both the statics as well as the dynamics. A flux of 6.6 x 10^8 ph/sec/(100 mA) of 9.0 keV x-rays, monochromated by the combination of a single-bounce mirror filter and a Ge monochromator, was incident on the sample. This resulted in about 100 times less incident x-ray flux than in our previous hexane/nitrobenzene experiments. A CCD area detector was used to measure the static x-ray scattering from the sample. It was also possible to use the CCD detector in XPCS measurements of the dynamics of concentration fluctuations in the mixtures, since the relaxations are quite slow due to the relatively high viscosity of the polymers.

The polystyrene/polybutadiene (PS/PB) polymer samples were mixed under air by weighing the components directly into the sample cell. The sample cell had a 3 mm long scattering volume with the entrance and exit windows covered by Be foils. The sample temperature was stable to within 1 mK during all measurements.

The dynamic data were collected in a sequence of 6000 exposures of the CCD. The exposure time for each frame was 0.15 seconds and the frame-to-frame time was 0.33 seconds. The total time for which the sample was exposed to x-rays during the sequence acquisition was around 900 seconds. During this time the sample was exposed to a radiation level of about 2000 kGy, which was below the x-ray radiation damage threshold experimentally determined for this sample. The x-ray scattering was collected over a CCD area of 180 x 180 pixels. At the detector-to-sample distance of 0.70 m, the pixel resolution was $q = 5.839 \times 10^{-5}$ Å^{-1}/pixel. The CCD was offset from the q = 0 position so that the q-range covered was from ~3.5×10^{-3} Å^{-1} to ~1.8×10^{-2} Å^{-1}. The data were collected and then analyzed offline using the custom written multitau correlation software, with 8 quasi-logarithmic correlators and 16 channels per correlator. The resulting correlation functions are shown in Fig. 6, where the solid lines represent single exponential fits. Several correlation functions were extracted for a few values of wavevector q and temperatures near the critical point. The contrast of the correlation functions, β, was between 1 and 3 %, similar to the values we found for the measurements on the hexane/nitrobenzene mixtures made using a single channel detector.

The fit values of the relaxation rates are plotted versus q for all three temperatures in Fig. 7. The manner in which the relaxation rate scales with wave vector depends on the conditions of the sample and way we probe it. These conditions can be characterized by the values of q, correlation length ξ, and the radius of gyration R_g, in terms of the values of $1/qR_g$, q , and q/R_g. The average value of the wavevector in our experiment was 5×10^{-3} Å^{-1}. The reduced temperatures range from 9.1×10^{-4} to 1.6×10^{-3}. For this range of reduced temperature, ξ is about 400 Å, as determined by fits of the scaling behavior of the amplitude and correlation length in our static scattering. An average value for R_g of the sample mixture is 9.2 Å. $N^{0.5}$ equals 4.4. Hence, the relevant physical regime is determined by the values $1/qRg = 21.7 > N^{0.5}$, $\xi/R_g = 43.5 > N^{0.5}$, and $q\xi = 2 > 1$. This puts the system in the so-called "critical non-diffusive" regime where mode coupling corrections dominate and the relaxation rate should scale with wave vector as $\Gamma \sim q^3$ and should be temperature independent, apart from the temperature dependence of the viscosity. While the measured values of Γ do increase with wave vector, they appear to increase much more quickly than q^3. Within the evident large scatter, the results for Γ are also approximately temperature independent.

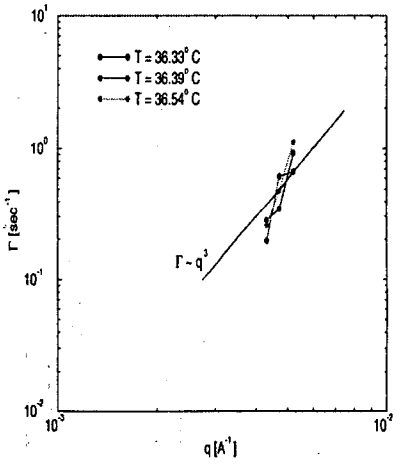

Fig. 7: Relaxation rate versus q.

The dynamic data we have been able to collect so far is not extensive enough to warrant drawing broader conclusions at this time. We will continue the experiments to gain additional insignts into this interesting system. We have demonstrated the ability to use XPCS to measure the relaxation rate from this polymer mixture and our work has identified a number of opportunities for enhancing the signal quality. This work forms part of the Ph.D. thesis of T. Nurushev (University of Michigan), see listing in Section 4.

2.4 *Coherent Bragg-rod Diffraction Studies of the Gd_2O_3 – GaAs Interface*

Y. Yacoby[1], R. Pindak[2], J. Pitney[2], R. MacHarrie[2], Eric M. Dufresne[3], E. Stern[4] and Roy Clarke[3]

[1] Racah Institute of Physics, Hebrew University, Jerusalem, Israel
[2] Lucent Technologies, Bell Laboratories, Murray Hill, NJ
[3] University of Michigan, Ann Arbor, MI
[4] University of Washington, Seattle, WA

Two-beam coherent diffraction [6] along Bragg rods is a powerful technique for the study of two-dimensional structures such as buried interfaces and aperiodic heteroepitaxial layer structures. Its advantage lies in the ability to extract directly both the amplitude and phase of the complex scattering factor, thereby enabling a direct determination of the structure by back Fourier transform (BFT). An important application of this method is to probe the atomic-level structure of the interface between a semiconductor wafer and a passivation layer deposited on its surface. In this particular experiment we are interested in the atomic structure of a 30Å Gd_2O_3 film epitaxially grown on the (100) surface of a GaAs single crystal.

The measurements were carried out in the following way: the sample was mounted on a 6-circle Kappa goniometer with the undulator x-ray beam vertically focused down to about 200 microns using a Rh-coated mirror. Reflection from this mirror, together with detuning of the second monochromator crystal, practically removed the third harmonic. The goniometer, the detectors and the slits were controlled by a Labview program that we developed. Special procedures were developed to line up the goniometer to the desired accuracy. The signal was measured using a scintillator-photo multiplier combination in the DC mode. This allowed us to measure signals as low as 50 counts/sec and up to 300,000 counts per second. The signal was normalized with respect to a reference signal and the background was subtracted.

The diffraction intensity was measured along a number of Bragg rods: (h 1 1), (h -1 1), (h 2 0), (h 2 2), (h 3 1), (h 3 3) in the range $0.5<h<3.5$. To analyze the data we start with a model structure and adjust its parameters to provide the best fit to all the Bragg rod intensities that were measured. Any discrepancies correspond to an unknown electron density that is the difference between the true electron density of the system and that represented by the model. We then calculated the complex scattering factor of the unknown electron density.

The results of this structure determination procedure are shown in Fig. 8 which illustrates BFT results obtained from a single Bragg rod (h 1 –1), representing the one-dimensional electron density profile in the direction normal to the interface. The electron density exhibits oscillations on the scale of a few monolayers, probably as a result of coherency strains due to the epitaxial mismatch. The next phase of this work is to measure the diffraction along all Bragg rods within a certain range in reciprocal space and perform a three-dimensional BFT to obtain the true three-dimensional electron density of the Gd_2O_3 passivation layer.

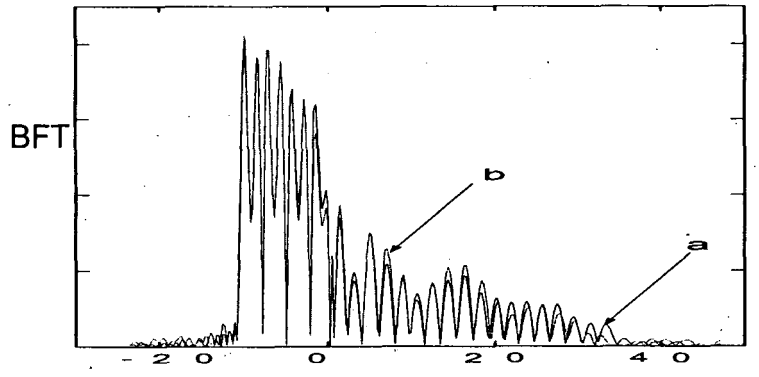

Fig. 8: Back Fourier transform of the complex structure factor of a 30 Å thick Gd_2O_3 passivation layer on (100) GaAs. Note the non-monotonic variations in the electron density to the right of the interface. The two curves (a) and (b) correspond to different starting models for the structure, illustrating that the final best fit BFT is relatively insensitive to the details of the initial reference model.

2.5. Instrumentation Development at 7-ID

In the first phase of MHATT-CAT's research covered by this grant MHATT-CAT beam line staff have been responsible for several important improvements to the Sector instrumentation. Much of this work was aimed at implementing new capabilities at the undulator line, for example the installation and commissioning of the pink beam filters in the first optics enclosure, 7-ID-A. This development is central to our x-ray photon correlation spectroscopy (XPCS) program, increasing the coherent flux on the ID line by over two orders of magnitude for those experiments that do not require a high degree of longitudinal monochromaticity (e.g., for XPCS studies of complex fluids, polymers and MR elastomers). This enables us to perform autocorrelation measurements down into the microsecond region, as demonstrated in MHATT-CAT's recent measurements on binary fluids [4].

Other instrumentation developments relate to the development of high resolution area detectors for time resolved x-ray scattering and small-angle XPCS. MHATT-CAT has developed a direct detection CCD camera in cooperation with a small company, CCD Direct, of Ann Arbor, MI. The camera uses radiation resistant virtual-phase CCD technology and is capable of operating at 15 frames per second with 12-bit dynamic range and a pixel size of 7 microns. We have also developed several imaging devices based on YAG crystal converters. These YAG imagers are installed at several locations on the beamline, particularly in the vicinity of the pink beam filters and the high heat load monochromator, for fast and convenient alignment of x-ray optics.

Many of the experiments that MHATT-CAT performs at Sector 7 have very demanding requirements on the brightness of the beam. An important instrumentation need therefore is for focusing optics of various kinds. In addition to reflective x-ray focusing optics MHATT-CAT has also been active in developing refractive optics: Li "alligator" lenses. These x-ray lenses are being developed in collaboration with a small company, Ecopulse Inc., Springfield, VA. The use of Li lenses is described in more detail below. MHATT-CAT partner, Lucent Technologies (Bell Labs) is also developing Bragg- Fresnel optics for microprobe work.

The following section details some of the instrumentation developments and upgrades performed under this grant.

2.5.1 *High Stability First Crystal Mount for Liquid Nitrogen Cooled Double Crystal Monochromator,* 7-ID-A.

Y. Yacoby, Hebrew University, E. Dufresne, University of Michigan, R. Pindak, Bell Labs, R. Clarke, University of Michigan.

During the period of this grant we have designed and installed a new high-stability crystal mount for the first crystal of our High Heat Load Monochromator (HHLM). We had been experiencing beam motion in our 7ID-C and D hutches on the order of 100 μm resulting from fluctuations (~0.2psi) of the pressure in the Oxford Cryocooler. Many beamlines at the APS have similar problems. This problem manifests itself also in a loss of flux during the LN_2 fill of the Cryocooler every three hours or so. We have now completely resolved this problem with the design shown in Fig. 9, This design is original and the work has been accepted for presentation at SRI 2001. The key aspect of the design is that it compensates the forces from pressure fluctuations by the use of symmetry in the LN2 flow. The new mount now flexes only by 0.2 μrad/PSI compared to 9.5 μrad/PSI with the old unit, an improvement by a factor 48 (Fig. 10). The total flux is now stable to about 0.35 % peak to peak over one hour.

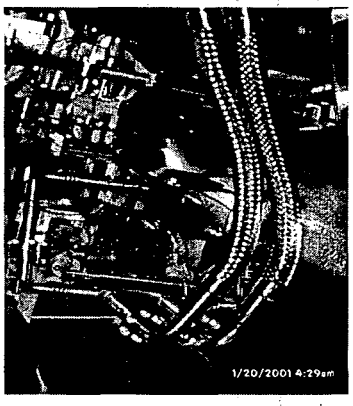

Fig. 9: New design for first-crystal Mount of liquid nitrogen cooled high heat load monochromator.

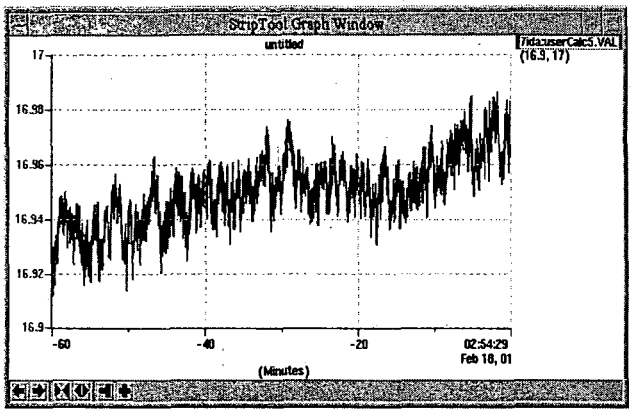

Fig. 10: Positional stability of monochromated beam after implementing new design. The RMS fluctuation is reduced to ~ 0.2 microradians per second at 100 mA beam current.

2.5.2. Refractive X-ray Optics for 7-ID-C and D.

Eric Dufresne and Steve Dierker, University of Michigan, **Nino Pereira**, Ecopulse, Inc. VA.

Another important instrumentation development under the current grant has been the first demonstration of Li-based Compound Refractive Lens focusing. We are developing these lenses in order to collect the horizontal fan of the undulator beam and increase the intensity in the 7ID-C and D hutches. Our ultrafast x-ray scattering experiments (Section 2.1) benefit greatly from a small intense x-ray spot size. In 2001, in collaboration with Dr. Nino Pereira from Ecopulse, Inc. VA (www.ecopulse.com), MHATT-CAT started to test Lithium as a possible material for x-ray lenses. Li has the potential for being the best material for such a lens in the energy range from 5-15 keV because it has the largest phase shift per unit absorption length of any solid. Dr. Pereira is an expert at handling Li, and has been making the lenses for us. Because Li tarnishes in humid air, we keep the Li in an evacuated container. We have found that is possible to keep the Li clean in this environment, and because Li is soft, we have found it easy to press it into the required lens shapes.

It has been shown recently by Cederstrom et al. [Nature **404**, 951 (2000)] that a periodic array of transmitting prisms can approximate a parabolic shape when the x-ray beam is incident at a small grazing angle to the teeth axis (see Fig. 11). This approach is simple and allows for changing the focal length with a simple angular tilt of the lens. For example, we will be able to focus the beam either in 7ID-C and D for different energies and either in the vertical or horizontal depending on the experiment requirements. We have recently tested these lenses in the 7ID-C hutch. Fig. 12 compares the unfocussed 10 keV X-ray beam 56 m from the source with a beam focused in the horizontal direction. The spatial variations in the unfocused beam profile are caused by the presence of Be and Kapton windows upstream in the beamline. The lens was a periodic array of 80 teeth, each with a 90 degree top angle, and a 1.5 mm pitch. Our lens was 7 m in front of the scintillator screen, coupled 1:1 to a 12 bit CCD camera. Theoretically, we would

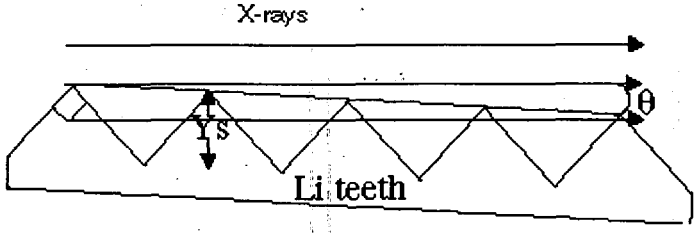

Fig. 11: Schematic of a single jaw of a Lithium "alligator" lens for x-ray beam focusing in 7-ID-C/D.

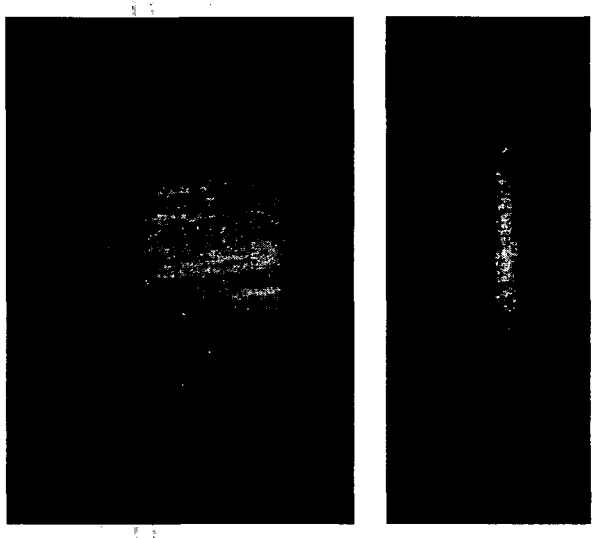

Fig. 12: Undulator x-ray beam focusing using Li-lens array. The unfocused beam on the left is ~1mm wide in the horizontal direction. After focusing (right) the beam narrows to 177 μm. The exposure time for image on the left is 6ms and for the one on the right1ms.

expect a gain of 5.2 and a FWHM close to 111 μm. We measured an intensity gain of a factor 3, and a 177 μm FWHM spot size. We believe the difference is due to the less than ideal surface figure of the teeth and Dr Pereira is currently working to improve the quality of his molds. Note that the lens transmitted 80 % of the X-rays which is comparable to the reflectivity losses from a typical grazing incidence X-ray mirror. We believe that an optical quality surface can be transferred to the Li by pressing a highly polished mold into the Li. It is very encouraging to find out that our first prototype here shows a gain of 3 already that can be used in an experiment.

On the strength of these results, Dr. Pereira was granted a Phase II SBIR grant to further develop Li-based x-ray optics. Access to beam time and the x-ray expertise at MHATT-CAT was instrumental in Ecopulse getting funding for this work. Already several groups around the world have started to contact him and are interested in possible collaborations. Dr Pereira gave a talk at the 2001 SPIE conference and our group also

contributed to several synchrotron radiation meetings on this topic. It is possible that commercial applications will result from this work.

3. List of Publications Resulting from this Grant.

Refereed Journals

1. "Coherent Control of Pulsed X-ray Beams", M.F.DeCamp, D.A. Reis, P.H. Bucksbaum, B. Adams, J.M. Caraher, **R. Clarke**, C.W.S. Conover, **E.M. Dufresne**, R. Merlin, **V. Stoica,** and J.K. Wahlstrand, Nature 413, 825-828 (2001).
2. "Probing impulsive strain propagation with x-ray pulses", D.A. Reis, M.F. DeCamp, P.H.Bucksbaum, **R. Clarke, E. Dufresne**, M. Hertlein, R. Merlin, R. Falcone, H. Kapteyn, M.M. Murnane, J. Larsson, T. Missalla, J.S. Wark, Phys. Rev. Lett., **86**, 3072-3075 (2001).
3. "3D X-ray crystal microscope" G.E. Ice, B.C. Larson, Adv. Eng. Mater. **2**, 643-646 (2000).
4. "A Study of Concentration Fluctuations in the Binary Mixture Hexane-Nitrobenzene with X-ray Photon Correlation Spectroscopy", **E. Dufresne, T. Nurushev, R. Clarke, S. B. Dierker**, Phys. Rev. E 65, June, 061507-1-061507-9, (2002).
5. "Elliptical x-ray microprobe mirrors by differential deposition", G.E. Ice, J.S. Chung, J.Z. Tischler and A. Lunt, Rev. Sci. Instrum **71**, 2635-2639 (2000).
6. "Direct structure determination of systems with two-dimensional periodicity", Y. Yacoby, R. Pindak, R. Macharrie and L. Pfeiffer, L. Berman, **R. Clarke**, J. Phys.-Condens. Mat. **12** 3929-393 (2000).
7. "Time-resolved x-ray diffraction from coherent phonons during a laser-induced phase transition", A. M. Lindenberg, I. Kang, S.L. Johnson, T. Missalla, P.A. Heimann, Z. Chang, J. L. Larsson, P.H. Bucksbaum, H.C. Kapteyn, H.A. Padmore, R.W. Lee, J.S. Wark, and R.W. Falcone, Phys. Rev. Lett. **84** (2000).
8. "Structural calibration of tensile-strained GaAs/InAlAs quantum wells", Q.R. Meng, T. Daniels-Race, W.P. Lowe Microw. Opt. Techn. Lett. **28**, 143-147 (2001).
9. "Ultrafast structural changes measured by time-resolved x-ray diffraction", J. Larsson, P.A. Heimann, A.M. Lindenberg, P.J. Schuck, P.H. Bucksbaum, R.W. Lee, H. A. Padmore, J.S. Wark, R.W. Falcone, Applied Phys. A Materials Science and Processing, **66**,587 (1998).
10. "Small-displacement monochromator for microdiffraction experiments", G.E. Ice, J.S. Chung, W. Lowe, **E. Williams** and J. Edelman, Rev. Sci. Instrum. **71**, 2001-2006 (2000.
11. "X-ray microdiffraction studies of mesoscale structure and dynamics below the size of most polycrystalline grains", G.E. Ice, J.-S. Chung, B.C. Larson, J.D. Budai, J.Z. Tischler and N. Tamura, and W. Lowe, accepted for publication in *Metal Physics and Advanced Technologies.*
12. "Ultrafast x-ray diffraction using a streak camera detector in averaging mode", J. Larsson, Z. Chang, E. Judd, P.J. Schuck, R.W. Falcone, P.A. Heimann, H.A. Padmore, H.C. Kapteyn, P.H. Bucksbaum, M.M. Murnane, R.W. Lee, A. Machacek, J.S. Wark, X. Liu, and B. Shan, Optics Lett. 22, 1012 (1997).
13. " Automated Indexing for Texture and Strain Measurements with Broad-Bandpass X-ray Microbeams", J.S. Chung and G.E. Ice, J. Appl. Phys. 86, 5249 (1999).
14. "Resonant X-ray Scattering at the Se edge in Liquid Crystal Free-standing Films and Devices", L.S. Matkin, H.F. Gleeson, P. Mach, C.C. Huang, R. Pindak, G. Srajer, J. Pollman, J.W. Goodby, M. Hind, A. Seed, Appl. Phys. Lett. 76, 1863-1865 (2000).
15. "Lithium lenses for x-ray refractive optics", **E. Dufresne, S. Dierker**, N. Pereira, Appl. Phys. Lett., **79**, 4085 (2001).

Refereed Conference Proceedings Publications

1. "Refractive and Reflective Optics for X-rays", N.R. Pereira, **E. Dufresne, S.B. Dierker, D.A. Arms**, to appear in Proc. Of the Dubna Synchrotron Radiation Conference 2001.
2. "Controlling Stress in Cubic Boron Nitride Coatings", **R. Clarke, D. Litvinov**, C. Taylor, D. Barlett, A. Inspektor, to appear in Proc. of International Conf. on Thin Films and Coatings, San Diego, CA, (2001). Thin Solid Films **398-9**, 137-141 (2001).
3. "Probing Relaxation in Magnetorheological Elastomers using X-ray Photon Correlation Spectroscpy", Proc. of International Conference on MR Materials, Nice, France (2001).
4. "3-D Measurement of Deformation Microstructure in Al(0.2%)Mg Using Submicron Resolution White X-ray Microbeams", B.C. Larson, N. Tamura, J.-S. Chung, G.E. Ice, J.D. Budai, J.Z. Tischler, W. Yang, H. Weiland and W.P. Lowe *MRS Fall Symposium Proceedings* (1999)
5. " Elliptical X-ray Microprobe Mirrors by Differential Deposition", G.E. Ice, J.-S. Chung, J.Z. Tischler and A. Lunt, AIP Conf. Proc. 1999 National Synchrotron Radiation Instrumentation Conf., Palo Alto, Ca. Oct. (1999).
6. " Design and Performance of X-ray Optics Optimized for Polycrystalline Microdiffraction", G.E. Ice, J.-S. Chung, B.C. Larson, J.D. Budai, J.Z. Tischler, N. Tamura and W. Lowe AIP Conf. Proc. 1999 National Synchrotron Radiation Instrumentation Conf., Palo Alto, Ca. Oct. (1999).
7. "X-ray microbeam measurement of local texture and strain in metals", J.-S. Chung, N. Tamura, G.E. Ice, B.C. Larson, and J.D. Budai, *Mat. Res. Soc. Symp.* **563** 169-174 (1999).
8. " Strain and Texture in Al-Interconnect Wires Measured by X-ray Microbeam Diffraction", N. Tamura, J.-S. Chung, G.E. Ice, B.C. Larson, J.D. Budai, J.Z. Tischler and M. Yoon *Mat. Res. Soc. Symp.* **563** 175-180 (1999).
9. " X-ray Microprobe for Fluorescence and Diffraction Analysis" G.E. Ice, to be published in Methods in Materials Research: A Current Protocols Publication, JohnWiley and Sons (1998).
10. "Application of combined white/monochromatic x-ray microbeam techniques for the study of texture and triaxial strain/stress in materials", N. Tamura, J.S. Chung, G.E. Ice, B.C. Larson, J.D. Budai, J.Z. Tischler, W.P. Lowe, Fall 1999 MRS Meeting Symposium (submitted).
11. "The use of x-ray microbeams in materials science", J.D. Budai G.E. Ice J.S. Chung, B.C. Larson, N. Tamura, J.Z. Tischler, D.P. Norton, W.P. Lowe, **E.L. Williams**, and P. Zschack, Proc. 9th Users Meeting of the Advanced Photon Source, Oct. 1998.
12. "A fixed-angle double mirror filter for preparing pink undulator beam at the Advanced Photon Source" **E. Dufresne, T. Sanchez, T. Nurushev, R. Clarke and S. Dierker**, AIP Conf. Proc. 1999 National Synchrotron Radiation Instrumentation Conf. Palo Alto, CA, Oct. (1999). Published in AIP Conf, Proc. 521, Melville NY, p238-241 (2000).
13. "Synchrotron X-Ray Microdiffraction Study Of Epitaxial Oxide Films On Textured Nickel Substrates", J. D. Budai, G.E. Ice, B.C. Larson, N. Tamura, J.S. Chung, J,Z. Tischler, D.P. Norton, **E.L. Williams**, W.P. Lowe, 1999 Denver X-Ray Conference (To Appear In Advances In X-Ray Analysis).
14. , "Lithum Metal for X-ray Filters and Refractive Optics", **D.A. Arms**, N.R. Pereira, **E.M. Dufresne, S.B. Dierker**, Proc. SRI 2001 Conference, August 2001.
15. **E.M. Dufresne, D.A. Arms, S.B. Dierker, R.Clarke**, Y.Yacoby, J.Pitney, R. MacHarrie, R. Pindak, "Design Performance of a Stable First Crystal Mount for a Cryogenically Cooled Si Monochromator at the APS", SRI 2001 Proc. (to be published).

16. N.R. Pereira, **D.A. Arms, R. Clarke, S.B. Dierker, E.M. Dufresne**, "Li Metal for x-ray Refractive Optics, SPIE 2001 Conference, July 2001 (INVITED Talk). To be published in SPIE Proc.

Conference Presentations

1. INVITED TALK: "Picosecond Time-Resolved X-ray Diffraction Probe of Coherent Lattice Dynamics" **D.A. Reis**, Synchrotron Radiation Instrumentation Conference SRI 2001, Wisconsin, Aug. 2001.
2. INVITED TALK: "In-situ Methods to Monitor and Control Stress in Thin Films", **R. Clarke**, Spring Meeting of the Materials Research Society, San Francisco, April 2001.
3. "Ultrahard Coatings based on Cubic Boron Nitride: in-situ Annealing and Stress Relief", **R. Clarke,** International Conference on Thin films and Coatings, San Diego, May 2001.
4. INVITED TALK: "The use of x-ray microbeams in materials science", J.D. Budai, G.E. Ice, B.C. Larson, N. Tamura, J.Z. Tischler, D.P. Norton, M. Yoon, W.P. Lowe, E.L. Williams, P. Zschack, 9th User's Meeting for the Advanced Photon Source.
5. "Crystallographic tilting of oxide films on textured metal substrates investigated by x-ray microbeams", J.D. Budai, N. Tamura, J.S. Chung, G.E. Ice, D.P. Norton, C. Park, J.Z. Tischler, B.C. Larson, A. Goyal, D. Lee, **E. Williams**, W.P. Lowe, 1999 APS March Meeting, Atlanta, GA.
6. "X-Ray Phase Determination In Two Dimensional Crystals", R. Pindak, Y. Yacoby, L. Pfeiffer, **R. Clarke**, 1999 APS March Meeting, Atlanta GA.
7. "X-Ray Microbeam Investigation Of Epitaxial Oxide Films On Textured Metal Substrates", J.D. Budai, N. Tamura, J.S. Chung, D.P. Norton, G.E. Ice, B.C. Larson, J.Z. Tischler, C. Park, D. Lee, **E.L. Williams**, W.P. Lowe, 1999 Mrs Spring Meeting, San Francisco, CA.
8. INVITED TALK: "KB mirror and scanning monochromator system for measuring strain in fine grained polycrystalline materials", Gene Ice, NSLS User's Meeting, May, 1999.
9. INVITED TALK: "Strain in al interconnects, N. Tamura, NSLS user's meeting", May, 1999
10. INVITED TALK: "Grain-by-grain microbeam studies of epitaxial growth of oxide films on vicinal substrates" J. Budai, NSLS User's Meeting, May, 1999.
11. "X-Ray Photon Correlation Spectroscopy of a Low-Molecular Weight Binary Fluid Mixture", **Eric Dufresne, Tim Nurushev, Roy Clarke, and S. Dierker**, X99 Conference, Chicago, August 1999.
12. "SAXS Study of Concentration Fluctuations in the Binary Mixture Hexane-Nitrobenzene", **T. Nurushev, E. Dufresne, R. Clarke, and S. B. Dierker**, American Physical Society March Meeting, Atlanta, GA, March 1999.
13. "Direct measurement of the time structure of ultrashort x-ray pulses from a storage ring", D. Walton, AIP Proc. 1999 National Synchrotron Radiation Instrumentation Conf. Palo Alto, CA, Oct. (1999).

4. PhD Theses based on work supported by this grant

"Investigation of solid-solid interface structure using a novel X-ray diffraction method".
M. Sowwan
Thesis Advisor: Prof. Y. Yacoby
Date of Graduation (Ph.D. degree) November 2002
Department of Physics, Hebrew University, Jerusalem, Israel.

"Seeing Sound: Dynamical Effects in Ultrafast X-ray Diffraction"
Matthew F. Decamp
Thesis Advisor: Prof. Phil Bucksbaum
Ph.D Thesis, The University of Michigan, 2002

"Studies of Static and Dynamic Critical Behavior of Simple Binary Fluids and Polymer Mixtures Using X-ray Photon Correlation Spectroscopy"
T.S. Nurushev
Thesis Advisor: Prof. S.B. Dierker
October 2000
Department of Physics, University of Michigan, Ann Arbor MI USA.