

# Sector 20 Time-Resolved XAFS

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## Introduction

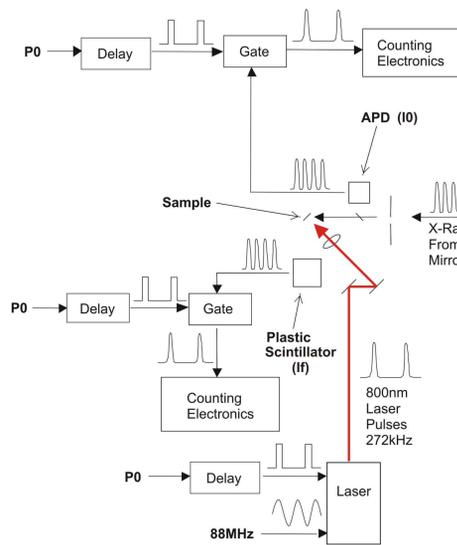
Investigation into the dynamics of materials employing a pulsed laser to pump the system into a highly non-equilibrium state and a fast probe to detect the resulting response is a very active field. Time-resolved XAFS utilizing the pulsed nature of a synchrotron source is a probe that is directly sensitive to the material lattice, is element specific, and does not depend on long-range order. The latter characteristic makes it an excellent choice to study dynamics of melting and/or amorphous and liquid materials. XAFS places stringent requirements on the signal-to-noise ratio, which is directly related to the measured x-ray flux, and therefore also the number of shots produced by the laser during the course of a time-resolved measurement. PNC/XOR has developed an apparatus based on a high rep/rate laser firing at the APS "P0" bunch repetition frequency of 272 kHz, allowing an increase in data collection efficiency by two orders of magnitude compared to typical pulsed laser systems, and a corresponding reduction in the time required for a typical experiment from weeks to hours. We have used this apparatus to observe the dynamics of laser-excited germanium films, with the ultimate goal of studying the melting dynamics, and the dynamics of laser-excited films of the optical phase-change material  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ .

## Laser System and Timing Electronics

The PNC/XOR system for time-resolved pump/probe XAFS experiments utilizes a Ti:Sapphire laser system that produces ~200fs pulses at a wavelength of 800nm, with repetition rate equal to the P0 clock rate (272kHz). This allows very high-efficiency XAFS measurements compared to most fs pulsed laser systems, which are limited to rep rates of ~1kHz. The time resolution of the system is primarily determined by the 100ps x-ray bunch width. An APD measures I0 and a fast, large-area plastic scintillator measures x-ray fluorescence from the sample. Amplified detector pulses are gated to select the signal from a single bunch, and relative timing between the laser pump pulse and x-ray probe bunch is controlled on a fine time scale by changing the phase of the RF reference used to synchronize the laser output to the ring.

## Schematic of the Time Resolved XAFS Apparatus

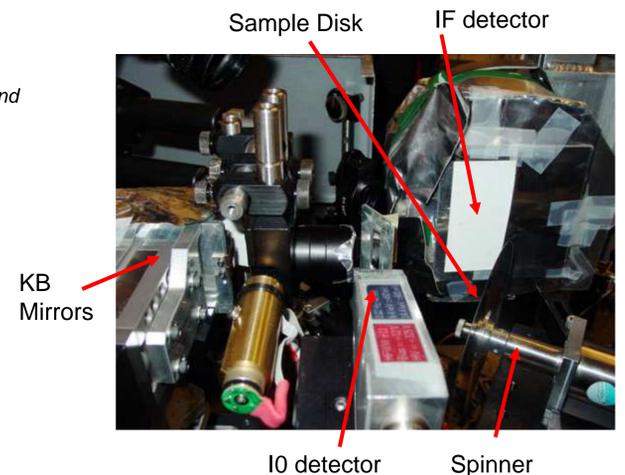
- 88MHz RF reference from ring (352MHz/4) syncs mode-locked seed laser to ring
- Delayed P0 signals trigger main laser amplifier, gates for fast detector pulses
- Timing changes are made by shifting phase of RF reference and/or changing trigger delay to pick up different seed pulse
- Gated detector pulses go to counting electronics.



## Laser-Excited $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Films

Preliminary experiments have been conducted on thin film structures similar to those used in actual DVD-RAM media. Results have been obtained in measurements of a film with a 50nm layer of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  on a  $\text{SiO}_2$  substrate, with a 50nm  $\text{SiO}_2$  cap layer. The sample structure was deposited on a disk and measurements were obtained with the disk spinning at ~1800 rpm. This reduced the effective sample exposure to the laser by a factor of ~6000 compared to a static experiment. This was done to reduce the potential for sample damage and the steady-state temperature buildup seen in the germanium film experiments. We find preliminary indications that we can observe a transition to a mixed liquid/crystalline state that occurs on the order of a few ns following laser excitation. Interestingly, we have observed that the film oxidized with laser exposure, even in a He/H atmosphere, above a fluence threshold of ~8 mJ/cm<sup>2</sup>, which excited ~8% of the available conduction band states. Our results have been included in an invited talk at the 2006 MRS meeting (2).

Closeup of sample setup, including view of the disk and spinner

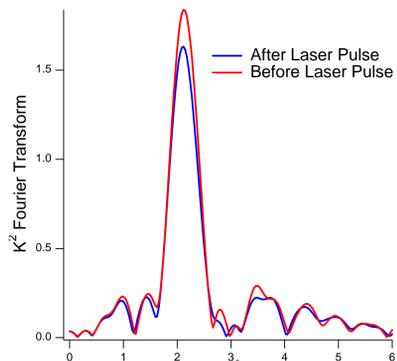


## Laser-Excited Germanium Films

Experiments have been conducted on 200nm germanium films. The ultimate goal is to study the dynamics of laser-induced melting, but this experiment has proven to be useful in understanding the issues involved in developing this novel apparatus, including stability of sample/beam alignment, build-up of an elevated steady-state temperature between shots, and sample damage over the time necessary to perform an experiment. Sample damage is probably due to slow evaporation at elevated temperatures and has prevented study of melting dynamics. This issue will be addressed by using the disk spinner developed for the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  experiments. APD detector arrays will decrease the time required for an experiment by about an order of magnitude.

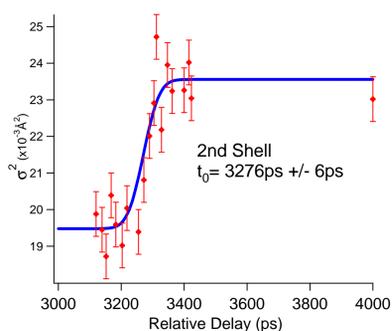
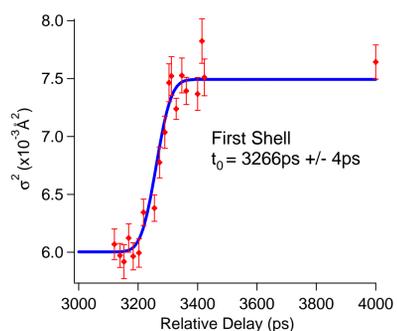
We have also obtained results for the time response to laser excitation of the EXAFS  $\sigma^2$  in the 1<sup>st</sup> and 2<sup>nd</sup> shells indicating a delay of ~10ps in the time response of the 2<sup>nd</sup> shell with respect to the 1<sup>st</sup> shell. This suggests a possible mechanism for excited carrier-phonon interaction producing the optical phonons to which the 1<sup>st</sup> shell is sensitive, which then equilibrate over a time period of ~10ps.

(1) E.A. Stern, D. Brewe, "Ultrafast XAFS Measurements on Laser Excited Ge Films," AIP Conference Proceedings, B. Hedman, P. Pianetta, eds., **882**, American Institute of Physics, February (2007), 24 - 28.

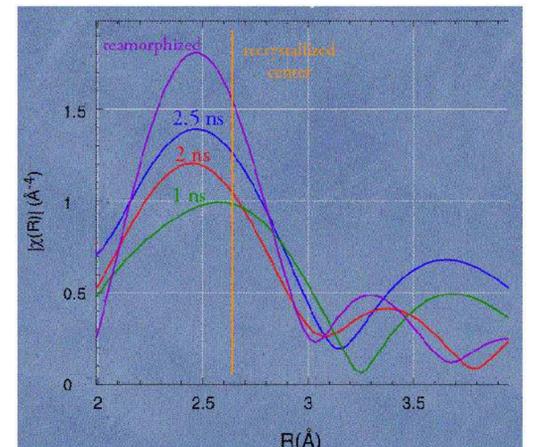


Left: Fourier Transformed EXAFS from germanium. The reduction in the peak is due to increased lattice vibrations that determine the EXAFS  $\sigma^2$ . Lattice vibrations contribute to  $\sigma^2$  of various shells differently, due to differences in the relative phase of atom pairs' motions in the vibrations. In germanium, the 1<sup>st</sup> shell is strongly sensitive to optical phonons, and very weakly sensitive to acoustic phonons.

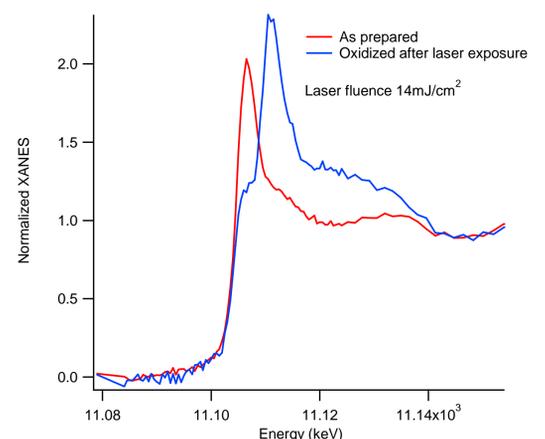
Below: The figures show 1<sup>st</sup> and 2<sup>nd</sup> shell  $\sigma^2$  vs. time in relative units, and the best-fit value for "t<sub>0</sub>", the relative time at which the sample response to laser excitation begins. Our results indicate a delay of ~10ps in the creation of vibrations to which the 2<sup>nd</sup> shell is most sensitive.



Fourier Transformed Ge EXAFS at several times after the laser pulse. The FT of the re-amorphized structure, which is similar to the liquid, is also shown (in purple). The orange line shows the position of the peak for the crystallized structure. These results appear to indicate a transition to a mixed crystalline/liquid state within a few ns of laser excitation.



Normalized XANES of the as-prepared film and after exposure to the laser. Under these conditions the film showed visual indication of change (increased scattering from film viewed in video camera) immediately upon exposure to the laser. We believe it's possible the film may be oxidized after even a single shot. This possibility may explain unusual results based on sample reflectivity that indicated 100fs laser pulses produced **much slower** amorphization than 30ps laser pulses in the related material GeSb (3). We plan to investigate this possibility in future experiments.



(2) Paul Fons, Dale Brewe, Ed Stern, A.V. Kolobov, Junji Tominaga, "Understanding Structural Changes in Phase Change Memory Alloys," Chalcogenide Alloys for Reconfigurable Electronics, MRS Proceedings Volume 918, A.H. Edwards, P.C. Taylor, J. Maimon, A. Kolobov, eds., **918**, Materials Research Society (2006),  
 (3) Wiggins et al., APL 84, 4445 (2004).

## Acknowledgments

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