**Contract No:**

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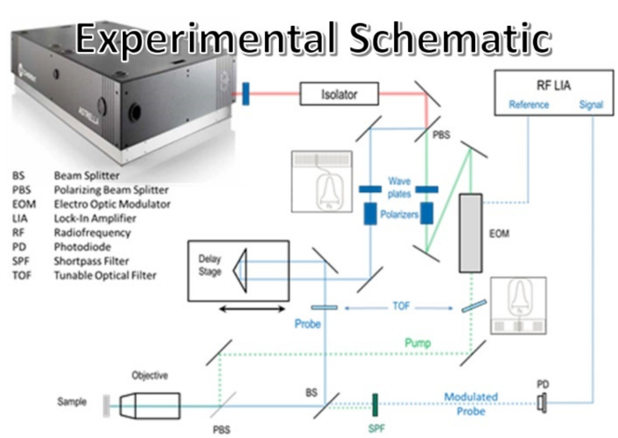
# Time Domain Thermoreflectance and Photodeflection Signatures of He Bubbles in Metals

The mechanical properties of materials steel and weldments for different components are affected by the radiolytic damage and expansion from helium bubbles to the crystal lattice. Periodic analyses of metals exposed to tritium gas are conducted to determine structural defects and temporal damage from tritium gas decay and He precipitation. Transmission electron microscopy (TEM) and autoradiography are the current analytical methods for the evaluation of metal damage. These methods are functional after several years of damage to the crystal lattice where $^{3}$He bubble formation damage can be seen with TEM. New analytical methods that can assess the damage to the crystal lattice early during the exposure to tritium are highly sought to ascertain the effects of material processing and tritium interactions. Further, simple sample preparation, compared to TEM, at a significantly reduced cost is highly desirable. A pump-probe laser technique using a femtosecond laser has been demonstrated to measure the thermal diffusivity in different materials. The time domain thermoreflectance (TDTR) laser setup can provide thermal diffusivity and phonon lifetime, which can be correlated with lattice damage. This advanced nonlinear optical technique will enable measurements of nanostructure damage in the metal before and after tritium exposure within a year. This report discusses current efforts in the design and development of the technique and the application to material characterization.




## Awards and Recognition

None.

## Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

## SRNL Legal Signature

9/2/20

**Signature** **Date**

# Time Domain Thermoreflectance and Photodeflection Signatures of He Bubbles in Metals

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Thrust Area: NS

Project Start Date: October 1, 2018
Project End Date: August 21, 2020

*The mechanical properties of the steel and weldments for different components are affected by the formation of helium bubbles as a result of tritium decay. Therefore, periodic analyses of metals exposed to tritium gas are conducted to determine structural defects and temporal damage from tritium gas decay and He precipitation. Transmission electron microscopy (TEM) and autoradiography are the current analytical methods for the evaluation of metal damage. These methods are functional after several years of damage to the crystal lattice where $^3$He bubble formation damage can be seen with TEM. New analytical methods that can assess the damage to the crystal lattice early during the exposure to tritium are highly sought to ascertain the effects of material processing and tritium interactions. Further, simple sample preparation, compared to TEM, at a significantly reduced cost is highly desirable. A pump-probe laser technique using a femtosecond laser has been demonstrated to measure the thermal diffusivity of different materials. The time domain thermoreflectance (TDTR) laser setup can provide thermal diffusivity and phonon lifetime, which can be correlated with lattice damage. This advanced nonlinear optical technique will enable measurements of nanostructure damage in the metal before and after tritium exposure within a year. This report discusses current efforts in the design and development of the technique and the application to material characterization.*

## FY2020 Objectives

- Demonstrate the concept of pump-probe laser setup for thermal characterization and phonon time domain to measure lattice damage.
- Demonstrate that a pump-probe laser experiment with a high repetition rate femtosecond laser can be used to characterize crystal lattice.
- Complete design and build experimental breadboard for time domain thermoreflectance (TDTR) and Transient Incoherent anti-Stokes Raman spectroscopy (TRIARS).
- Acquire tritiated samples and test materials with known damage in a clean laboratory.

## Introduction

Periodic analyses of reservoirs filled with tritium are conducted at the Tritium Facility to determine the effects of tritium to the stainless steel and the temporal damage from He precipitation (Figure 1a). The mechanical properties of the walls and pinch weld of the tritium vessels are affected by the tritium decay resulting in the formation of He bubbles (Figure 1b). Transmission electron microscopy (TEM) and autoradiography are the current analytical methods for the evaluation of the reservoir metal. These methods are functional after several years of damage to the crystal lattice where $^3$He bubble formation damage can be seen with TEM (Figure 1c and d). New analytical methods that can assess the damage to the crystal lattice early during the exposure are highly sought to ascertain the effects of material processing and tritium interactions. Further, simple sample preparation, compared to TEM, can be done at a significantly reduced cost. An ultrafast pump-probe laser technique is a potential innovative approach to this problem, where only 20 µm of material is required for analysis.

The time domain thermoreflectance (TDTR) technique will enable measurements of nanostructure damage in the metal before and after tritium exposure within a year. If this work is successful will result in significant savings to the program (short turnaround analysis) and could help provide new directions for research on new materials, effects of processing, metal coatings and new designs for tritium storage systems. This work is also applicable to other tritium production and storage products, such as tritium-producing burnable absorber rods (TPBARS). This new technology will enhance SRNL's reputation as the leader for tritium storage research through years to come, which can result in significant funding from NNSA Weapons Programs. This report discusses current efforts in the design and development of the TDTR technique and the application to material characterization.

## Approach

Paddock *et al.* [1] in 1986 demonstrated for the first-time thermal diffusivity measurements from thin metal films using picosecond transient thermoreflectance to measure the thermal properties of metal films as thin as 100 nm. The thermal conductivity of the material is based on an ultrafast heating pulse inducing a change in the index of refraction of the material, and therefore a change in the optical properties. The ultrafast pump-probe technique is a two-laser beam technique that depends on one laser for heating the surface (pump), while another laser probes the heating effect on the material via reflection (Figure 1). Technology has evolved using a femtosecond laser instead of a picosecond laser, different colors for the pump and probe (better discrimination) and the optical modulation of the laser beam to enhance the signal-to-noise ratio. Additional improvements have been added with the interference of two optical beams reflected from the front surface and scattering depth. These improvements have resulted in the understanding of thermal properties of nanoparticles with dimensions less than 10 nm. Other variants include the ultrafast demagnetization of a sample while probing its recovery, such as the magneto-optical Kerr effect.

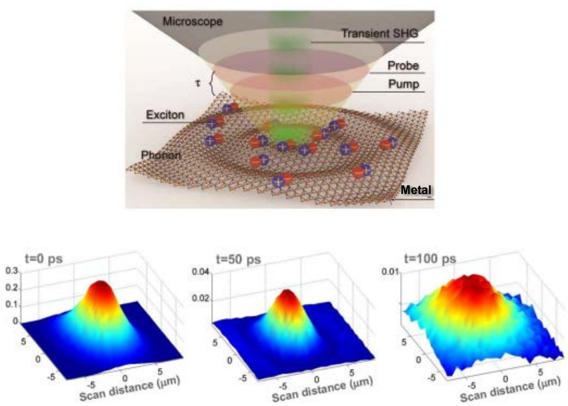


**Figure 1.** The pump-probe temporal surface dynamics.

The advances in pump-probe laser technologies can be used to demonstrate the detection and quantification of damage in materials. The beta decay of tritium results in the formation of $^3$He, which precipitate in bubbles. The $^3$He precipitates damage the metal crystal lattice producing phonon scattering points. Phonons (collective excitation in a periodic, elastic arrangement of atoms or molecules in condensed matter) produced during the laser heating pulse travels through the crystal lattice until thermalization. The presence of defects in the lattice shortens the phonon lifetime. This effect will be valuable to determine the crystal lattice damage by the beta decay and precipitation of He bubbles.

Since metals do not show Raman bands, the best option is to measure the phonon lifetime based on thermal conductivity. Previous work by Weisensee *et al.* [2] measured the effect of ion irradiation on the thermal conductivity of $UO_2$, and $U_3O_8$ using TDTR. Thermal conductivity measurements via TDTR were also used to characterize radiation-induced damage of ZIRLO [3], a low oxidation Zircaloy, and in silicon. Lattice impurities have been shown to affect the thermal conductivity of materials. For instance, oxygen impurities changed the thermal conductivity of beta-$Si_3N_4$ [4] from 120 W/m-K to 88 W/m-K. The same techniques can be used to study acoustic and optical phonons in a material.

## Results/Discussion

A TDTR setup was assembled on a laser table adjacent to the Astrella laser to take advantage of the Vitara oscillator laser (80 MHz, 35 fs) embedded within the Astrella laser system. Our TDTR setup was developed as a two-tint pump-probe technique, meaning the pump and probe wavelengths are split into two beams from a single broadband beam and the wavelengths of the two beams are only separated by ~10 nm [5]. In addition, to the assembly and alignment of the TDTR setup, programming to control the delay stage, lock-in amplifier and spectrograph is underway. Thermal code is also being written to extract thermal conductivity and capacitance information from the collected TDTR data. Figure 2a shows the schematic of our TDTR setup and Figure 2b shows a photo of our actual laboratory setup.

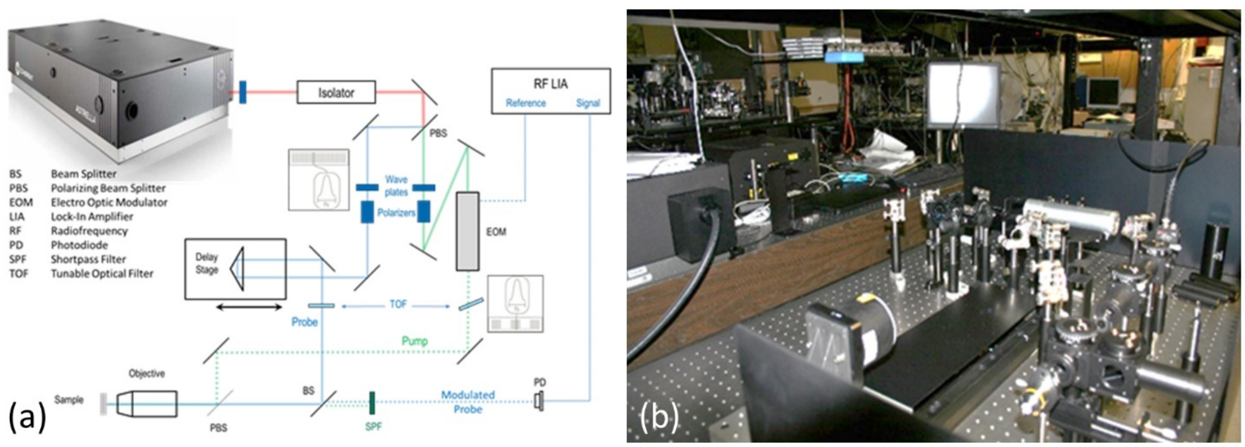


**Figure 2.** (a) Pump-probe experimental setup (TDTR) under development and (b) actual pump-probe TDTR experimental setup under development.

A sample cell tested by the SRNL/Defense Programs to transport tritiated materials in an inert, argon atmosphere was selected as a sample holder for this program. A plan for the transfer of tritium-loaded samples to a clean laboratory was discussed with Radiological Protection and was approved. A sample from PNNL containing tritium was also received for this program.

## FY2020 Accomplishments

- Covid-19, technical problems with the laser, and early termination of the LDRD project affected significantly the outcome and results of this project.
- Different TDRD and TRIARS setups were designed for this project.
- A system based on a single broadband wavelength laser with two filters (two-tint) was chosen for this project.
- Components for TDRD breadboard were procured and assembled

- The TDRD setup was assembled next to the Astrella laser to take advantage of the embedded 80 MHz, 35 fs oscillator laser.
- Initial laser beam alignment through the TDRD system was completed.
- Programming to control stage, lock-in amplifier and spectrograph is underway.
- A tritiated sample in argon atmosphere was brought for analysis.
- Discussions with the Tritium Facility resulted in the preparation of samples with tritium for delivery to SRNL.
- Modulation of the laser beams and observation of the modulation was measured with a lock-in amplifier.
- A coherent anti-Stokes Raman spectrometer setup was modified for TRIARS measurements.

## Future Directions

- The thermal conductivity and capacitance will be measured for several materials to ensure the instrument is properly calibrated.
- After the repair of the Vitara laser, the equipment will be used for NA22 funded project.
- Samples with known dosage and time exposed to tritium will be investigated.

## FY 2020 Publications/Presentations

1. None

## References

1. C.A. Paddock and G.L. Eesley, "Transient thermoreflectance from thin metal films", *J. Appl. Phys.*, 60 (1), **1986**, 285-290.
2. P.B. Weisensee, J.P. Feser, and D.G. Cahill, "Effect of ion irradiation on the thermal conductivity of $UO_2$ and $U_3O_8$ epitaxial layers", *J. Nucl. Mater.*, 443, **2013**, 212-217.
3. R. Cheaito, C.S. Gorham, A. Misra, K. Hattar, and P.E. Hopkins, "Thermal conductivity measurements via time-domain thermoreflectance for the characterization of radiation induced damage", *J. Mater. Res.*, 30(09), **2015**, 1403-1412.
4. H. Yokota and M. Ibukiyama, "Effect of lattice impurities on the thermal conductivity of β-$Si_3N_4$", *J. Eur. Ceram. Soc.*, 23(1), **2003**, 55-60.
5. K. Kang, Y.K. Koh, C. Chiritescu, X. Zheng, and D.G. Cahill, "Two-tint pump-probe measurements using a femtosecond laser oscillator and sharp-edged optical filters", *Rev. Sci. Instrum.*, 79, **2008**, 114901.

## Acronyms

ASL – Advanced Spectroscopy Laboratory
He – Helium
TDTR – Time Domain Thermoreflectance
TEM – Transmission Electron Microscopy
TPBARS – Tritium-Producing Burnable Absorber Rods

## Intellectual Property

None.

## Total Number of Post-Doctoral Researchers

1 Post-Doctoral Researcher (Don D. Dick), on-Site at SRNL.