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Time Resolved Spectroscopy Using Synchrotron Infrared Pulses

G. L. Carr[†], R. P. S. M. Lobo[†‡], C. J. Hirschmugl[§], J. LaVeigne[‡],
D. H. Reitze[‡], and D. B. Tanner[‡]

[†]National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973-5000
[‡]Physics Department, University of Florida, Gainsville, FL 32611
[§]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

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National Synchrotron Light Source
Brookhaven National Laboratory
Upton, NY 11973

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G.L. Carr[†], R.P.S.M. Lobo[†‡], C.J. Hirschmugl[§], J. LaVeigne[‡], D.H. Reitze[‡], and D.B. Tanner[‡]

†National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973
‡Physics Department, University of Florida, Gainesville, FL 32611
§Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Abstract

Electron synchrotron storage rings, such as the VUV ring at the National Synchrotron Light Source (NSLS), produce short pulses of infrared (IR) radiation suitable for investigating time-dependent phenomena in a variety of interesting experimental systems. In contrast to other pulsed sources of IR, the synchrotron produces a continuum spectral output over the entire IR (and beyond), though at power levels typically below those obtained from laser systems. The infrared synchrotron radiation (IRSR) source is therefore well-suited as a probe using standard FTIR spectroscopic techniques. Here we describe the pump-probe spectroscopy facility being established at the NSLS and demonstrate the technique by measuring the photocarrier decay in a semiconductor.

Keywords: pump probe spectroscopy, picosecond spectroscopy, photocarrier decay, Ti:sapphire laser, far infrared.

Introduction

Pump-probe is a well-established time resolved spectroscopy technique that avoids the problems of poor sensitivity that usually accompany sampling or gating a fast detector. Typically, an experimental specimen is excited by a short duration pulse of light (the "pump"), and a subsequent pulse of light (the "probe") spectroscopically senses the specimen. The two pulsed sources are synchronized, but with the probe arriving a controllable time delay Δt after the pump. Thus, the pump serves to excite the specimen while the probe senses the specimen's state at Δt after the pump. The process can repeat at a rapid rate, resulting in high signal throughput and good signal-to-noise using high sensitivity spectrometer and detector systems. This is particularly true for the helium-cooled bolometric detectors commonly used for the far infrared spectral region which can have time constants measured in 10s of milliseconds. The standard MCT photoconductive detector for mid-IR spectroscopy has a time constant on the order of 1 μs. Faster MCT photodiodes have recently become available but typically do not perform as well beyond 10 μm wavelengths (presumably due to material difficulties associated with narrow gap p-type MCT). In any event, the required wide bandwidth electronics introduce additional noise. All these aspects motivate the use of the pump-probe technique for the infrared. Obviously, the technique requires two sources of pulsed light having qualities appropriate for photoexciting a specimen and spectroscopically sensing it. We consider such sources below.

Pulsed Infrared Sources

In a typical laboratory-based set up, both the pump and probe are provided by laser systems, and the time resolution is determined (or limited) by whichever pulse is longer. Short (< 1 ns) pulse lasers are available which can be used for this purpose[1], but with certain limitations. Mode-locked lasers operate primarily in the near-IR and visible spectral ranges, with the Ti:sapphire laser being among the best known due to its wide tuning range and extremely short pulses. Non-linear mixing techniques, such as the optical parametric oscillator (OPO) can extend the output range of these laser systems to the mid-IR. The long-wavelength limit of such systems is about 20 μm, due to absorption and phase matching difficulties in existing non-linear crystal materials.

Techniques for generating short pulses at longer wavelengths have recently evolved, again based on short-pulse near IR lasers like Ti:sapphire. The so-called "coherent THz pulses"[2] have durations of a few picoseconds

and spectral content extending from centimeter waves up to ~100 μm, though most of the energy occurs near 300 μm. This spectral range matches the absorption by mobile charge carriers in a number of semiconductor systems, and coherent THz pulses have been successfully used for pump-probe spectroscopy of photocarriers in III-V materials[3].

Free electron lasers (FELs) naturally produce a pulsed output when driven by an rf linear accelerator, and pulse durations of less than 1 ps can be achieved[4]. The extremely high power and brightness are the primary motivations for their construction. Though they can be designed for operation in the far, mid, or near IR, they are not well-suited to spectroscopy over a wide spectral range, and their stability may not be sufficient for some spectroscopy applications.

The synchrotron is another accelerator-based source of infrared[5]. Again, acceleration is achieved with an rf-system that bunches the electrons, and a pulsed output of a few 10s to 100s of picoseconds is typical. Synchrotron radiation is emitted as the electrons traverse the bending magnets that keep the electrons circulating in a closed orbit. Though the brightness of the synchrotron source is much lower than for FELs and conventional lasers, it is still several orders of magnitude greater than for thermal spectroscopy sources. Two other important attributes are its continuum spectral output across the entire infrared (and beyond) and good stability, which allows the use of highly refined FTIR (Fourier Transform Infrared) spectrometry instrumentation. The good stability stems, in part, from the non-resonant (non-stimulated) emission mechanism and also the fact that the same electrons circulate for long periods of time, i.e. there is no shot-to-shot noise that can occur in FELs. The integrated average power across the infrared is measured in milliwatts, so the synchrotron source is not well-suited to the task of photoexcitation except when high sensitivity systems (e.g. detector materials or devices) are being investigated.

Pump-Probe Spectroscopy with Synchrotron Infrared at the NSLS

As noted above, the synchrotron infrared source has a number of desirable qualities for performing spectroscopy, especially time-resolved spectroscopy. The VUV ring at the National Synchrotron Light Source (NSLS) has supported an infrared spectroscopy program at beamline U4IR since the late 1980s. Among those measurements, several have made use of its pulsed output[6], including pump-probe spectroscopy in conjunction with a Nd:YAG laser[7,8]. A second infrared beamline (U12IR) is nearing completion and will support the majority of near-term time-resolved studies. We will describe only those features of U12IR that are relevant to the time-resolved program. A full description of that and other new infrared beamlines will be presented elsewhere[9].

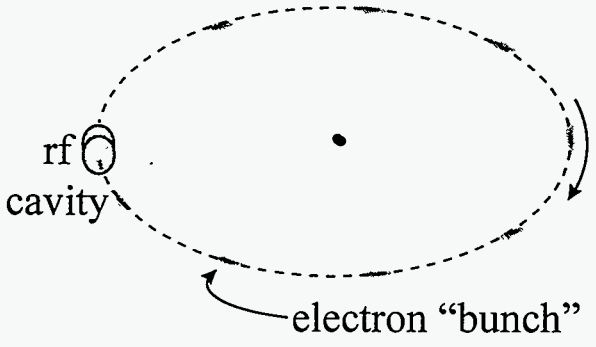

Figure 1. Schematic of synchrotron operation showing electron bunching. Only 8 of 9 possible rf "buckets" are shown filled.

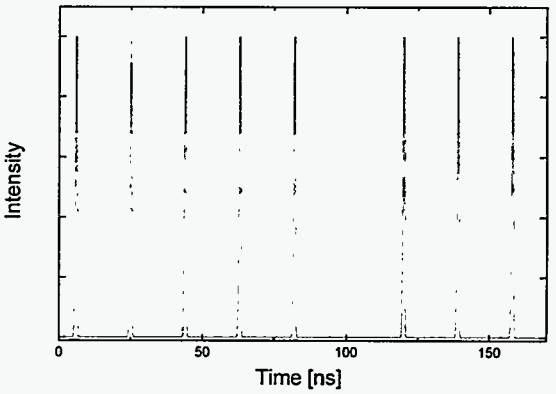

Figure 2. Pulse pattern that would result when 8 of 9 buckets are filled.

The NSLS VUV ring operates with a 52.9 MHz rf system which is compatible with electron bunches spaced at 18.9 ns intervals. Electrons orbit the 51 m circumference ring in 170 ns, during which time the rf cycles 9 times. Therefore, the ring can support up to 9 bunches of electrons, each in a so-called rf "bucket". It is not necessary to fill each rf bucket, and other bunch patterns can be introduced. Since our goal will be to

synchronize the pulses from the ring with another (non-synchrotron) pulsed source, the symmetric 9, 3, and 1 bunch patterns are the most useful. Thusly, the available pulse repetition frequencies (PRFs) from the synchrotron are 52.9 MHz, 17.6 MHz, and 5.88 MHz. The pulse duration depends on the length of an electron bunch, which in turn depends on the synchrotron's operating conditions. Pulse widths in the 1ns range are typical, but special configurations are expected to provide pulses as short as 100ps.

Synchrotron IR Beamline and Spectrometry

Two interferometer endstations at beamline U12IR will span the far and mid-IR spectral regions: a Bruker IFS113v and a lamellar grating interferometer[10]. The Bruker 113 spans the range from ~20 cm^{-1} to beyond 3000 cm^{-1}, while the lamellar is optimized for the range from a few cm^{-1} up to 50 cm^{-1}. Interferometers can attain high spectral resolution when operated with a large optical path difference. However, this causes concern when used for a time-resolved measurement, especially when the time difference associated with this path difference exceeds the pulse width. This is a possibility since the Bruker's ~ 0.1 cm^{-1} spectral resolution is achieved with an optical path difference of ~20 cm; a distance greater than a 3 cm long, 100 ps infrared pulses from the VUV ring. One concern stems from the standard practice of placing the sample after the interferometer. In this situation, the interferometer divides the infrared probe pulse in two and separates them in time, leading to an ill-defined pump-to-probe delay time at the sample. Placing the sample before the interferometer is a remedy for situations where this could be a problem. The other concern, that the FTIR spectrometer would never produce any interference when the pulses did not physically overlap in space (or time), is not a problem. A specimen possessing a narrow spectral feature naturally brings about a coherence time that can exceed the pulse separation, allowing interference to occur. The situation is actually no different than for a CW source having a coherence length much shorter than the optical path difference (the usual case).

For the majority of the IR spectral range, the synchrotron infrared will be transported with conventional mirror optics, resulting in minimal pulse dispersion. One exception concerns wavelengths in the millimeter region for which light pipe (cylindrical metal tubing) is used to overcome the diffraction losses that accompany conventional sized optics. Like multi-mode step-index optical fibers, light pipe suffers from modal dispersion. For meridional rays, the dispersion for light entering within a cone of half-angle θ is given by $\Delta t=(L/c)[(\cos\theta)^{-1}-1]$. Light propagating at f/3.5 or above will experience 100 ps or less dispersion in a 3 meter length of pipe. We estimate that only frequencies below 7 cm^{-1} will fill the pipe at > f/3.5, with 2 cm^{-1} light experiencing a maximum of 400 ps dispersion. Indeed, since we are approaching the low frequency cutoff of 1.27 cm diameter light pipe, we expect that such long wavelengths will propagate only in low order modes, tending to minimize the degree of modal dispersion.

Pump Laser System

Though there are many types of pulsed laser systems, the choices for performing sub-nanosecond spectroscopy at 10 to 100 MHz PRFs are rather limited. Mode-locked lasers are the obvious choice for achieving both short pulse widths and high PRFs. Of these, Nd:YAG and Ti:sapphire can be mode-locked with PRF's in the 80 MHz range. Typically, a Nd:YAG laser ($\lambda = 1.064$ μm) produces greater power, but lacks tunability although useful power can be obtained by frequency doubling, tripling, etc. in non-linear crystals such at KTP. Pulse durations are between 50 and 100 ps. Such a system was previously implemented elsewhere[11] as well as at the NSLS[7]. A wider tuning range can be achieved by optical parametric oscillators (OPOs), but not at the high PRFs necessary for matching the synchrotron.

Mode-locked Ti:sapphire lasers provide excellent tunability, and can be efficiently frequency doubled to achieve tunability across nearly ½ of the visible spectrum. The power levels are somewhat lower, and the range of PRFs is a bit more restricted, than for Nd:YAG. But pulse durations are generally much shorter, ranging from a few picoseconds down to below 100 fs.

One other laser system that deserves mentioning is the solid state diode laser. Depending on packaging and device architecture, some of these diodes can be switched on and off at multi-MHz rates. The challenge is to

produce and deliver the necessary high peak current, short duration pulses to these non-linear, low impedance devices.

Two types of laser systems have been established at the NSLS. The primary system is a mode-locked Ti:sapphire laser, specially built[12] to operate using the VUV ring's 52.9 MHz rf signal, and producing pulses at a 105.8 MHz repetition frequency. This is twice the multi-bunch pulse frequency for the IR from the VUV ring, so a custom "divide-by-two" pulse selector will be used to match the multi-bunch IR pulse pattern. Another pulse selector will provide divide-by-three and divide-by-nine to match the two other symmetric bunch patterns that the ring can support. The 52.9 MHz rf signal is produced from a pick-up loop directly on the synchrotron's rf cavity, rather than the rf drive signal, since the former is expected to provide better phase fidelity with respect to the electron bunches. The laser can be pumped with either an Ar^+ or frequency-doubled $Nd:YVO_4$. The tuning range for the fundamental is from ~0.7μm to ~1μm, with an output power of 1 to 2 watts. For reasons to be described below, we have chosen a laser designed to produce 2 ps (rather than femtosecond) duration pulses.

The laser control system ("synchro-lock") allows for external signals to be introduced, such as phase shifting so as to adjust the time delay between the pump (adjustable) and probe (fixed) pulses. By applying a square or sine wave signal, the pump-to-probe delay time can be modulated and lock-in detection techniques employed. This naturally rejects "static" (i.e. thermal) effects that are susceptible to drifts, allowing small time-dependent absorption signals to be extracted from beneath otherwise large, temperature-dependent absorption features. A schematic of the system is shown in Figure 3. The upper limit on useful modulation frequencies is determined by the infrared spectrometer detector. In the far infrared, these are typically liquid-helium cooled bolometers with time constants of a few milliseconds, and modulation frequencies of 100 to 200 Hz can be employed.

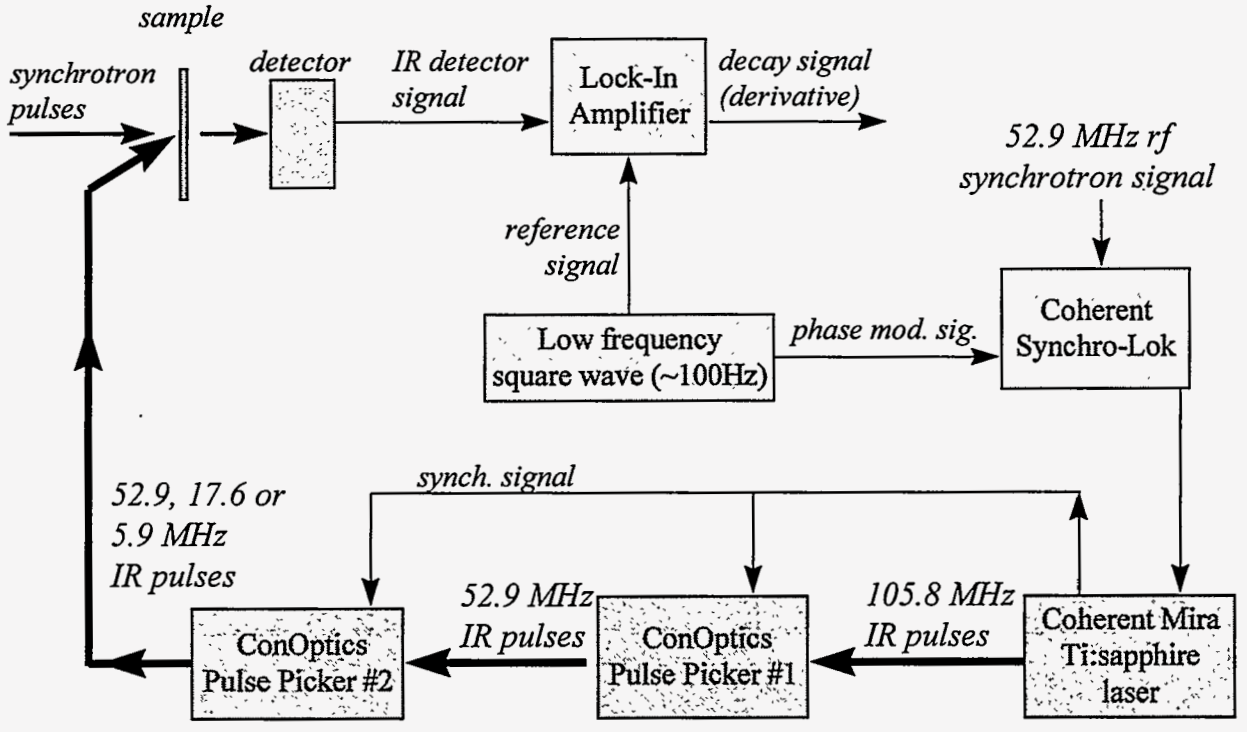

Figure 3. Schematic of electronic and optical system for bringing synchronized laser and synchrotron pulses to a sample in a time-resolved spectroscopy measurement. The time delay between pump and probe is modulated at ~100 Hz, and lock-in detection is used to extract only time-dependent signals.

In addition to the Ti:sapphire laser, a synchronized Ga(Al)As laser diode system has also been developed. The diode is driven by a custom electronic system based on a fast pulse generator (< 1 ns transition times), a wide-band rf power amplifier, and a pulse transformer / bias network. With this system, nearly 1 W (peak power) IR pulses can be produced at 52.9 MHz or 5.88 MHz with pulse durations of approximately 1 ns. The particular laser diode[13] has an essentially fixed photon energy of 845 nm. We note that the electronic pulse system (without the diode) could be used for direct electrical excitation of some sample systems to perform "electrically pumped, optically probed" time-resolved spectroscopy. The electronic system is readily triggered by the synchrotron rf signal.

Pulse transport

The NSLS VUV ring supports many beamlines, including several for infrared spectroscopy. Fiber optic cable will be used to distribute the laser pulses to a particular beamline. We have chosen graded-index multi-mode fiber since it can handle greater power and simplifies the coupling of light into the fiber (as compared to single-mode optical fiber). Graded-index fiber is necessary (as opposed to step-index) for minimizing modal dispersion of the pulses to below 0.2 ps/m. Intrinsic dispersion, due to the dependence of refractive index on wavelength for glass, must also be considered. For 2 ps duration, transform limited pulses at 850 nm wavelength, the dispersion will be 0.12 ps/m. This increases to more than 2 ps/m for 100 fs laser pulses. The dispersion becomes even more important for frequency-doubled Ti:sapphire. At a wavelength of 450 nm, even 2 ps duration pulses will disperse at nearly 4 ps/m while 100 fs pulses experience ten times this value. Since we anticipate fiber lengths less than 50 m, modal dispersion is well under control. To minimize intrinsic (material) dispersion, we have chosen a Ti:sapphire laser that produces ~2 ps duration pulses (as opposed to one that delivers femto-second pulses). For those situations where pulse dispersion still limits the technique's time-resolution (e.g. when using frequency-doubled Ti:sapphire pulses through 50 m optical fiber), dispersion compensation can be employed.

Since we do not anticipate pulse widths from the synchrotron much shorter than ~ 100 ps, the ability to characterize the pulses at substantially better time resolution is not necessary. Fast photodiodes and digital oscilloscopes with < 25 ps rise and fall times are available for the near IR and visible spectral range. Since the synchrotron output includes the entire IR and visible ranges, both pump and probe sources can be characterized, and synchronized, to an accuracy of a few 10s of picoseconds with the same photodiode detection system.

Example Measurement Results

To illustrate the capability of pulsed synchrotron infrared for pump-probe spectroscopy, we have conducted a measurement of the photocarrier decay in semi-insulating (SI) GaAs. The measurement was performed using the Ga(Al)As diode laser system with a limiting time resolution of ~ 1 ns. The induced far-IR absorption was analyzed in terms of mobile photogenerated carriers, from which a carrier scattering rate and conductivity were extracted. The results are shown in Figure 4. The scattering rate is time dependent, changing from an electron dominated value to a hole dominated value within 20 ns of the pump pulse. This indicates that the electron lifetime is extremely short compared to the hole lifetime. An interpretation based on surface states and band bending has been developed and will be presented elsewhere.

Summary

A facility for performing sub-nanosecond time-resolved spectroscopy by the pump-probe method has been greatly improved at the NSLS. The pump sources include synchronized Ti:sapphire and GaAs diode lasers. The pulsed synchrotron radiation serves as the probe, and its continuum spectral output spans the entire infrared range, allowing high resolution spectroscopy to be performed with standard FTIR instrumentation. We demonstrate the method by measuring the photocarrier decay in a semiconductor system, and extract useful information on carrier type that would be difficult to obtain by an electrically sensed measurement.

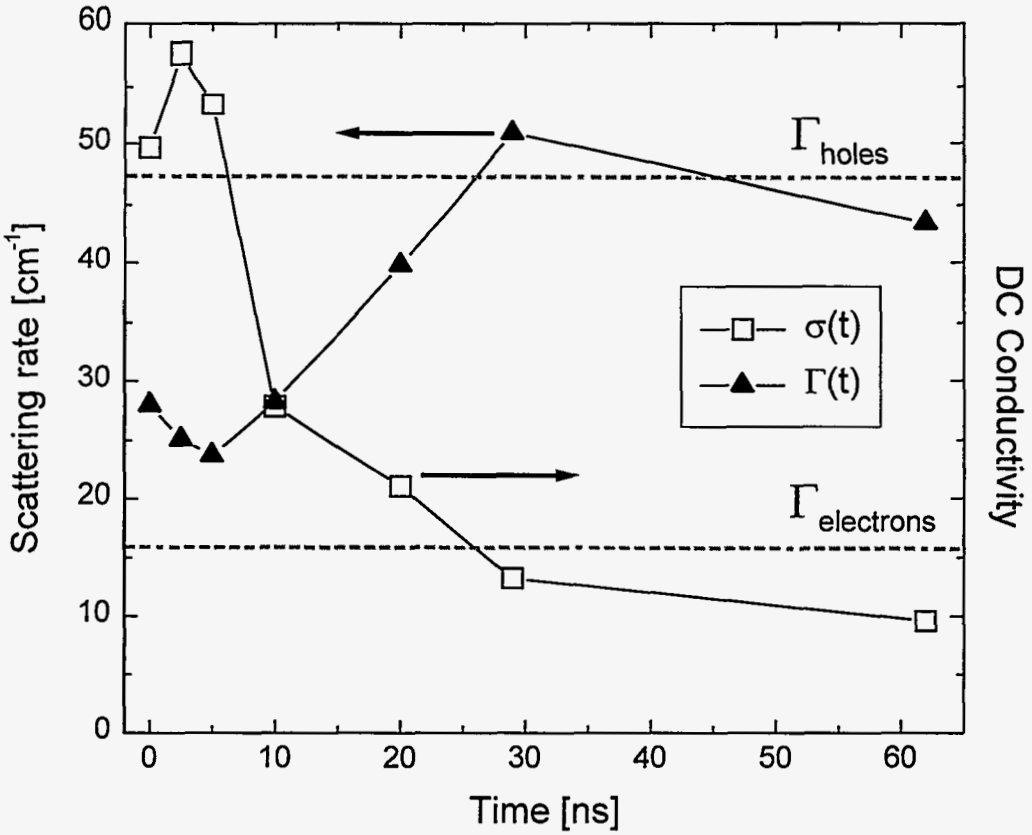

Figure 4. Time-dependent photocarrier scattering rate (Γ) and photoconductivity (σ) extracted from fits to the far infrared transmission through a wafer of GaAs.

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