Two-tint pump-probe measurements using a femtosecond laser oscillator and sharp-edged optical filters

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We describe a simple approach for rejecting unwanted scattered light in two types of time-resolved pump-probe measurements, time-domain thermoreflectance (TDTR) and time-resolved incoherent anti-Stokes Raman scattering (TRIARS). Sharp edged optical filters are used to create spectrally distinct pump and probe beams from the broad spectral output of a femtosecond Ti:sapphire laser oscillator. For TDTR, the diffusely scattered pump light is then blocked by a third optical filter. For TRIARS, depolarized scattering created by the pump is shifted in frequency by $\approx 250\ \mathrm{cm}^{-1}$ relative to the polarized scattering created by the probe; therefore, spectral features created by the pump and probe scattering can be easily distinguished. © *2008 American Institute of Physics.*
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I. INTRODUCTION

Since the advent of mode-locked lasers,[1] pump-probe optical measurements have been widely used to study the ultrafast dynamics of optical, electronic, and chemical processes. More recently, variations of this technique have been developed to determine the thermal and mechanical properties of thin films, interfaces, and nanostructures.[2] In a typical pump-probe optical measurement, a pump optical pulse generates some type of excitation in the sample and the temporal evolution of this excitation is tracked by measuring changes in the transmitted or reflected probe optical pulse as a function of the time delay between the pump and probe.

These changes in the probe signal are typically small and considerations of dynamic range of the detector usually demand that light originating from the pump beam be rigorously excluded from the detector. In some cases—for example, when a probe beam is specularly reflected from a smooth surface—the probe beam can be adequately separated from the pump beam using different optical paths combined with orthogonal polarizations for the pump and probe. On the other hand, when sample roughness or inhomogeneities produce a significant amount of diffusely scattered light, the reflected or transmitted pump light cannot be easily separated from the probe by geometry and polarization alone. For these reasons, the use of different wavelengths of light for the pump and probe, i.e., a two-color pump-probe approach, is advantageous.

Two-color pump-probe measurements can be implemented in many ways. A common approach is frequency doubling of either the pump or the probe beam by a nonlinear crystal.[3–5] Optical parametric amplifiers (OPAs),[6,7] optical parametric oscillators,[8] and supercontinuum generation[9] have been widely used to create tunable sources. For example, Katayama and Kawaguchi[9] used supercontinuum generation and optical bandpass filters to produce spectrally distinct pump and probe beams. Recently, two mode-locked lasers operating at different wavelengths have been synchronized[10,11] electronically. A two-color pump-probe approach provides high rejection of diffusely scattered pump light but adds significant complexity to the apparatus.

We describe a simple way to achieve high rejection of scattered pump light without the use of a nonlinear element or an additional laser cavity. Our approach is to employ sharp-edged optical filters to form spectrally distinct pump and probe beams from the high and low frequency ends of the broadband output of a Ti:sapphire laser oscillator. Since the pump and probe wavelengths are separated by only ≈ 10 nm, we refer to this approach as a "two-tint" method. In Secs. II A–II C, we describe two implementations of this idea for time-domain thermoreflectance (TDTR)[2,12–14] measurements of thermal transport properties and time-resolved incoherent anti-Stokes Raman scattering (TRIARS).[6,15–17]

The two-tint method has the following technical advantages over conventional two-color methods: (1) No additional alignment of the optical system is needed. (2) The two-tint method avoids the increased fluctuations in laser power that result from frequency conversion by nonlinear optics;[18] since noise in both the pump and probe beam affect the signal-to-noise (SNR) ratio[19] of a pump-probe measurement, two-color methods that adopt nonlinear optics will typically reduce the SNR. (3) In the two-tint method, the pump and probe powers are linear in the incident laser power and independent of repetition rate; frequency conversion by OPAs typically requires pumping by an amplified, low repetition-rate source laser. (4) The two-tint method avoids photodegradation by keeping both the pump and the probe in the near infrared. One of the most common ways of producing a traditional two-color measurement is to frequency double either the pump or the probe but the resulting UV photons can sometimes damage photosensitive samples.

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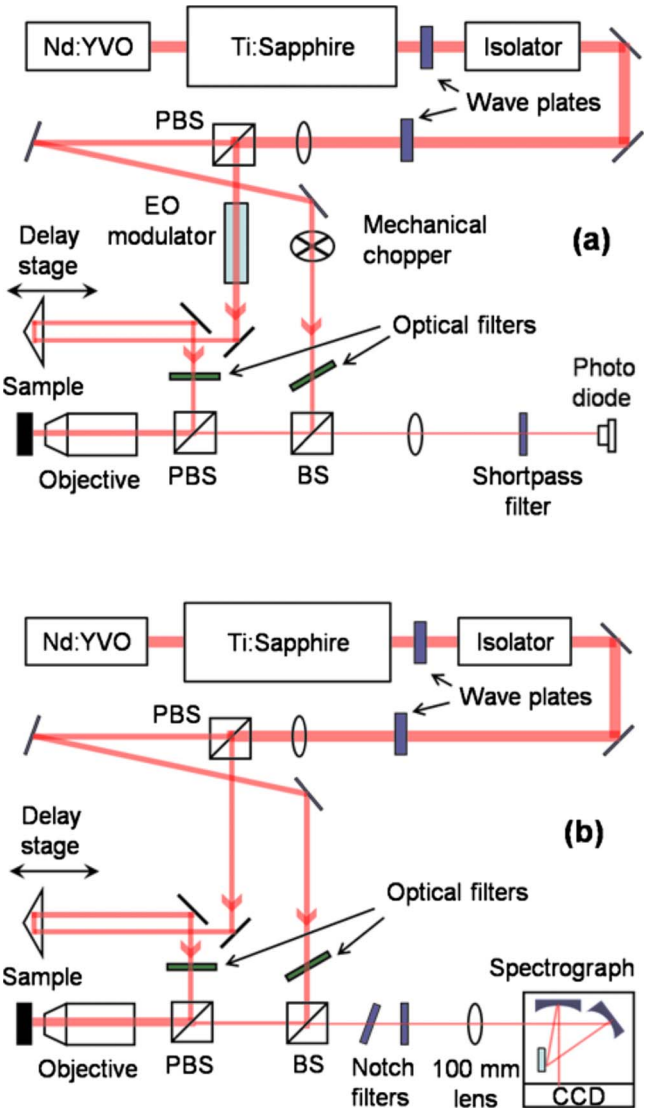

FIG. 1. (Color online) Schematics of the optical layouts for two-tint pump-probe measurements of (a) TDTR and (b) TRIARS.

II. IMPLEMENTATION OF THE TWO-TINT PUMP-PROBE METHOD

A. General features

Figure 1 illustrates the placement of the optical elements in the layouts of TDTR and TRIARS experiments. The laser output first passes through a $\frac{1}{2}$-wave plate and optical isolator that also serves as a power control. The second $\frac{1}{2}$-wave plate and polarizing beam splitter (PBS) control the relative amount of laser power that becomes the pump and probe beams. The pump beam is formed by the reflection of *s*-polarized light from the PBS. In the TDTR setup, the pump beam then passes through an electro-optic modulator. In both cases (TDTR and TRIARS), the pump beam is reflected by a retroreflector, passes through an optical filter, and is reflected by a second PBS before entering the microscope objective. The position of retroreflector is adjusted by a variable delay stage to advance the pump beam relative to the probe.

The probe beam is formed by the beam transmitted through the first PBS and steered by two mirrors and a nonpolarizing beam splitter through the second PBS and into the microscope objective. An optical filter is placed in front of the nonpolarizing beam splitter. The pump and probe are cross polarized. In the TDTR experiment, the pump and probe beam paths are parallel but separated vertically by ≈5 mm at the back focal plane of the objective. The reflected or scattered light is collimated by the microscope objective. The PBS behind the objective blocks most of the light that is polarized perpendicular to the plane of the optical table but a significant fraction of the reflected or scattered light from the pump beam can still pass through the PBS due to the finite extinction ratio of the PBS, birefringence in the sample or optics, and depolarized light scattering.

B. Time domain thermoreflectance

There are many possible permutations on the selection of the three optical filters in a TDTR measurement. We have found the following configuration convenient: (i) a long-wave pass optical filter with a cutoff of 790 nm is placed in the path of the pump beam; (ii) a bandpass filter with center wavelength of 785 nm and a bandwidth of 3 nm—i.e., a transmission band of 785 ± 1.5 nm—is placed in the path of the incident probe; and (iii) a short-wave pass optical filter with a cutoff of 780 nm is placed in front the photodetector. We then adjust the laser oscillator to produce a center frequency of 785 nm and a full width at half maximum (FWHM) bandwidth of 12 nm. Finally, the bandpass filter in the probe path is tilted to maximize the signal on the photodiode detector; the peak wavelength of the probe is then at ≈781 nm. (Titling the filter blueshifts the center frequency of the bandpass filter; for the filters we are using, a tilt angle of 13° creates a wavelength shift of 5 nm.) This procedure separates the peak wavelengths of the pump and probe intensities by ≈10 nm, see Fig. 2(a). Diffuse pump light scattered from the sample is suppressed by a factor of ≈1000, see Fig. 2(a).

The pulse duration of a Ti:sapphire laser oscillator is typically bandwidth limited but the duration of the pump and probe optical pulses are substantially broadened by the large dispersion of the isolator and the electro-optic modulator. (Our isolator is composed of 21 mm length of terbium gallium garnet crystal and 16 mm length of one calcite polarizer. The entire isolator has a group delay dispersion (GDD) of 6000 fs^2. Our electro-optic modulator in the pump optical path is constructed from a 160 mm length of potassium dideuterium phosphate (KD^*P) and has a GDD of 7500 fs^2.) Therefore, the insertion of optical filters into the beam paths lengthens the duration of the probe pulses but actually reduces the duration of the pump pulses. The reduction in the duration of the pump pulses is more significant and the overall time resolution is improved with this configuration of optical filters, see Fig. 3(a). Data for the time correlations of the pump and probe at the position of the sample are easily acquired by placing a GaP photodiode at the sample position and connecting the output of the detector to the input of the rf-locking amplifier.

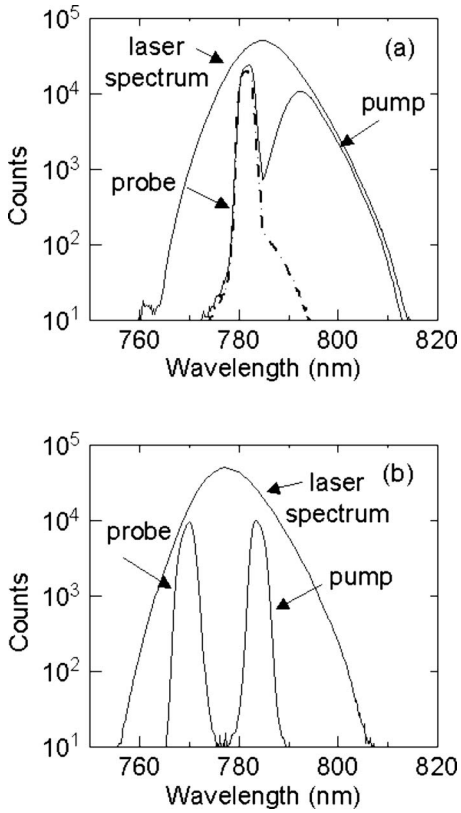

FIG. 2. (a) Spectral intensities in the two-tint pump-probe measurements of TDTR. The output of the laser is sliced at either side by two optical filters to create the pump and probe beams. A third optical filter blocks diffusely scattered pump light from reaching the detector. The solid and dashed lines are the spectral intensities before and after the third optical filter, respectively. (b) Spectral intensities in the two-tint pump-probe measurements of TRIARS.

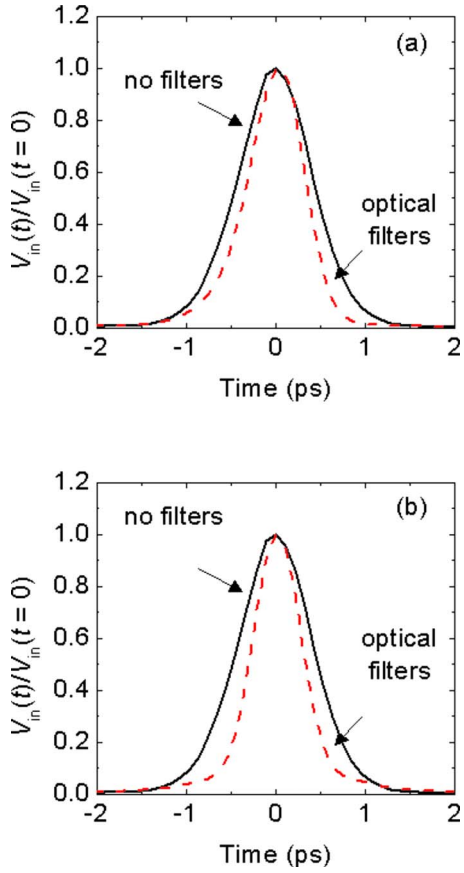

FIG. 3. (Color online) Time correlations of the pump and probe optical pulses in the two-tint pump-probe measurements of (a) TDTR and (b) TRIARS. The solid and dashed lines are the pump-probe correlations without and with optical filters, respectively. The FWHM of the pump-probe correlation without filters is ≈0.9 ps, and the correlations with filters in the measurement of TDTR and TRIARS are ≈0.75 and ≈0.65 ps, respectively.

C. Time-resolved incoherent anti-Stokes Raman scattering

In a TRIARS experiment, we place two laser-line filters with transmission bands of 785 ± 1.5 nm in the paths of the pump and probe beams. The laser-line filter in the path of the probe beam is tilted until the peak intensity of the probe shifts to 770 nm. We then tune the laser oscillator to a central wavelength of 777 nm and a bandwidth of 10 nm. This procedure separates the peak wavelength of the probe from the peak wavelength of the pump by 15 nm, see Fig. 2(b), corresponding to a frequency shift of ≈250 cm^{-1}. The spectral widths of the pump and probe pulses are 50 cm^{-1} FWHM. For this configuration of optical filters, the pump-probe correlation is ≈0.7 ps, see Fig. 3(b).

Figure 4 shows the anti-Stokes Raman spectra for a thin layer of carbon nanotubes deposited onto a sapphire substrate. The delay time between the pump and probe for these data is $t=0.4$ ps and the pump and probe fluences are 175 and 140 $\mu J\ cm^{-2}$, respectively. Two distinct features are observed in the anti-Stokes range of 1230–1680 cm^{-1}. The peak in the spectra centered at −1580 cm^{-1} is due to Raman scattering by the G mode optical phonon (OP) created by probe beam. The peak in the spectra centered at 1330 cm^{-1} is due to depolarized Raman scatterings by the G mode OP created by the pump beam. The G mode Raman intensity created by pump is weaker than the intensity created by probe because polarized Raman scattering by pump beam is mostly blocked by the polarizing beam splitter, see Fig. 1. Because the G mode Raman peak created by probe beam is well separated from the Raman peak created by pump beam, see Fig. 4, we are able to track the evolution of G mode OP population by simple integration of the Raman intensity created by probe beam measured at each delay time t. Detailed

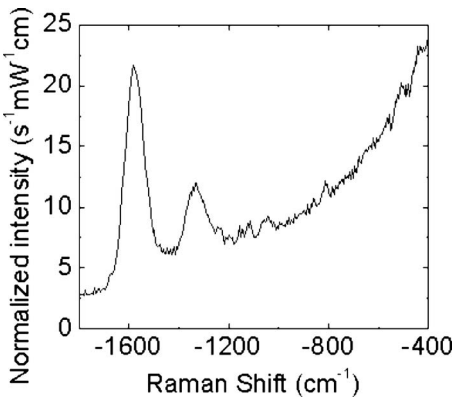

FIG. 4. Anti-Stokes Raman spectra for arc-discharge carbon nanotubes created by both pump and probe optical pulses. Raman intensity is normalized by the integration time, power in the probe beam and spectral width of one charge coupled device pixel.

analysis of OP lifetimes in arc-discharged nanotubes were performed in Ref. 15.

III. CONCLUSION

In conclusion, we presented a simple two-color pump-probe approach that employs two optical filters to create spectrally distinct pump and probe beams from the relatively broad spectrum of the laser oscillator. With this novel technique, the Raman scattering created by probe beam is spectrally separated from the scattering created by pump beam in TRIARS. This technique can be used to remove the unwanted diffuse scattered pump signal from samples with rough surfaces in TDTR measurements.

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