

## Broadband Coherent anti-Stokes Raman Spectroscopy Characterization of Polymer Thin Films

Coherent anti-Stokes Raman scattering (CARS) alleviates restrictive conditions of surface enhanced Raman scattering (SERS) because nonlinear mixing occurs throughout the focal overlap region of the incident beams and is not dependent upon substrate enhancement. NIST researchers have demonstrated a simple modification to an existing nonlinear spectrometer that enables CARS characterization of thin polymeric films. We find that this methodology permits rapid acquisition of high signal-to-noise (S/N) spectra. Indeed, broad-bandwidth CARS spectroscopy has been demonstrated to have clear sensitivity advantages over conventional Raman spectroscopy for the characterization of thin films. The spectroscopy shows special promise for the characterization of the ultrathin organic films required for advanced electronic applications such as organic light emitting diodes and thin film transistors.

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The advent of robust, ultrafast lasers has enabled the application of coherent nonlinear spectroscopies to routine sample characterization. Coherent anti-Stokes Raman scattering, CARS, is the nonlinear equivalent of conventional spontaneous Raman scattering. Conventional Raman is a scattering process, and the signal is highly dependent upon collection efficiency. The coherent nature of the CARS process gives rise to a directional signal simplifying collection and improving the sensitivity. Surprisingly, there has been little work exploring the utility of CARS as a thin film diagnostic. Surface enhanced Raman scattering, SERS, has been used to probe the interfacial region of thin polymer films on metal surfaces. However, limitations inherent in SERS leave much unknown. For example, SERS enhancement often requires roughened coinage metal (Au, Ag, Cu) substrates. It is difficult to characterize film surface interactions when enhancement only comes from particular surface sites. Additionally, SERS enhancement only extends a few nm into the film, making it sensitive to the interface, but blind to contributions from further into the bulk.

A schematic of a typical, degenerate CARS experiment is given in Figure 1. Two laser pulses are incident on the sample, with frequencies  $\nu_1$  and  $\nu_2$ . They mix nonlinearly to give an output pulse at the frequency  $\nu_3=2\nu_1-\nu_2$ . If the difference frequency  $\delta=\nu_1-\nu_2$  is resonant with a Raman active transition in the sample, the mixing process is enhanced and a vibrational spectrum can be recorded. In the NIST experiments, a 100 femtosecond pulse duration laser is used to generate a broadband packet of frequencies at  $\nu_2$ ;

this provides high peak fields, improving the nonlinear mixing, and simplifies the data collection by reducing the need to tune the laser providing  $\nu_2$ .

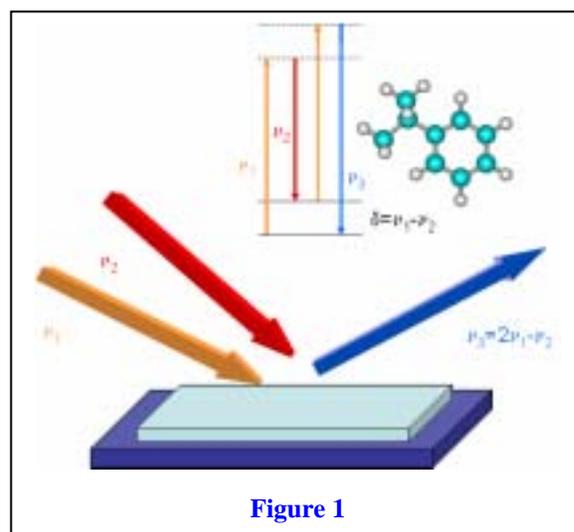


Figure 1

Experiments were performed with a variety of thin polymer film samples to establish the potential of broad-bandwidth CARS in comparison with conventional Raman spectroscopy.

Figure 2 is a comparison of a CARS spectrum of a 138 nm PS film (upper) to a conventional Raman spectrum of the same film (lower).

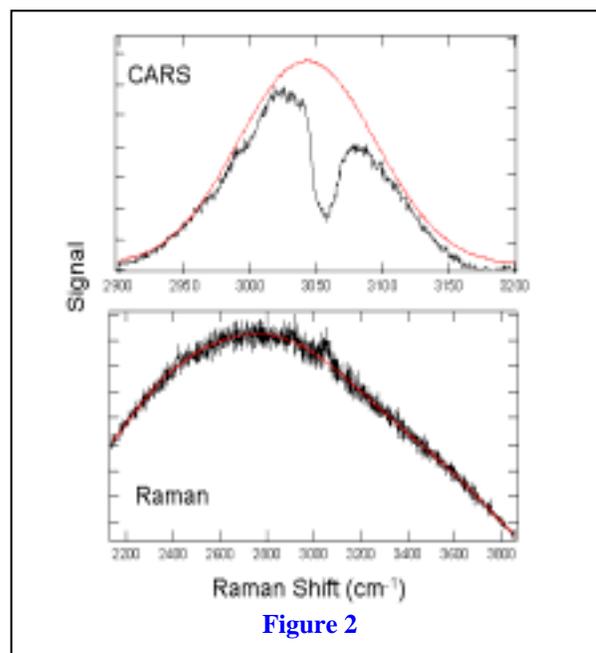


Figure 2

Shown in the lower panel of **Figure 2** is the Raman spectrum of a 138 nm polystyrene,  $-\text{[CH}_2\text{CHC}_6\text{H}_5\text{]}_n-$ , film, recorded with a 633 nm laser and a commercial Raman collection system. The weak feature at  $3060\text{ cm}^{-1}$  is the Raman active fully symmetric stretching vibration of the 5 C-H bonds on the phenyl ring ( $\text{C}_6\text{H}_5$ ; see schematic in Figure 1). The broad background is due to fluorescence from both the polymer and the Si substrate. Shown in the upper panel of Figure 2 is the CARS spectrum of the same film. For the CARS measurement, the polystyrene (PS) vibrational features appear as ‘anti resonances’ on a non-resonant background. Both the conventional and CARS spectra in Figure 1 were taken with identical acquisition times (60 s) and comparable total power onto the sample. The CARS spectrum is clearly of much higher quality. Quantitative analysis of the data indicates that CARS measurement displays a  $\approx 25$  times improvement in the S/N.

Additional experiments for films of various polymers have been performed on diverse substrates (Si, Au, glass). The film thickness was varied from  $\approx 20$  nm to  $\approx 300$  nm. In all cases, high quality vibrational spectra were acquired, with demonstrated improved S/N compared to conventional Raman spectra.

A mathematical framework for the quantitation of the CARS spectra, accounting for the influence of the substrate dielectric response, was developed and shown to be consistent with the measurements.

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**Future Plans:** In addition to providing chemical structure information, via the vibrational spectrum, the CARS scattering process is exquisitely sensitive to both the symmetry and orientation of the sample. Standard procedures to quantify these aspects of the sample, via detailed polarization studies, will be developed and verified.