

### Time-reversal invariance and Raman measurements of phonon populations under nonequilibrium conditions

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The use of the Stokes-to-anti-Stokes Raman intensity ratio to infer a phonon population in an absorbing solid is complicated by absorption effects and by the frequency dependence of the cross section. We show that the time-reversal invariance of the Raman cross section may be used to obtain both correction factors even under nonequilibrium conditions. The technique is illustrated by measuring phonon populations in Si under laser-annealing conditions.

It is well established that the ratio of Stokes-to-anti-Stokes phonon Raman scattering may be used to infer phonon temperatures in a solid.<sup>1</sup> However, when this ratio is used in a strongly absorbing solid such as a semiconductor above the band gap, it is important to correct for the frequency dependences of the absorption coefficient and of the resonance Raman cross section.<sup>2</sup> In many cases the spectral dependence of the absorption coefficient is well known, but for only a few solids have the resonance effects in the Raman cross section been mapped over a wide spectral range.<sup>3</sup> Thus, these correction factors are often unknown even at room temperature and seldom are they available over the range of sample temperatures necessary to fully exploit the Raman signals as a probe of lattice temperature.

In recent work our group has been interested in the use of Raman temperature probes under highly nonequilibrium conditions such as occur during pulsed laser annealing of semiconductors.<sup>4</sup> Under these situations there exist almost no data at all on these correction factors. In this paper we shall

demonstrate how the time-reversal invariance of the Raman cross section may be exploited to obtain, via Raman scattering, the required corrections *under exactly the conditions for which the temperature or phonon population is sought*. The technique involves a set of three Raman intensity measurements—only one more than needed for the temperature measurement itself. The method requires the use of a tunable dye laser and will be illustrated for pulsed-laser-excited silicon.

The Stokes Raman-photon-generation rate  $R_S$  at frequency  $\nu_S$ , in the backscattered direction from the thickness element between  $z$  and  $z + dz$  below the surface is given by

$$dR_S(z) = \nu_S^3 R_L e^{-\alpha_L z} \sigma(\nu_L, \nu_S) [n(z) + 1] dz, \quad (1)$$

where  $R_L$  is the incident laser photon flux,  $\alpha_L$  is the absorption coefficient at the laser frequency  $\nu_L$ ,  $\sigma(\nu_L, \nu_S)$  is the Stokes Raman cross section, and  $n(z)$  is the phonon occupation factor. The total signal leaving the sample is

$$R_S = \nu_S^3 R_L \int_0^d \{ \sigma_S(\nu_L, \nu_S, z) [n(z) + 1] \times \exp[-(\alpha_L + \alpha_S)z] \} dz \quad (2)$$

where  $\alpha_S$  is the absorption coefficient of the scattered Stokes light and  $d$  is the sample thickness. It is often possible experimentally to obtain a Raman probe depth  $(\alpha_L + \alpha_S)^{-1}$  which is much smaller than the characteristic length for variation of the phonon population or Raman cross section. Under these circumstances and for  $d \gg (\alpha_L + \alpha_S)^{-1}$ ,

$$R_S = \frac{\nu_S^3 R_L \sigma_S(\nu_L, \nu_S) (n + 1)}{\alpha_L + \alpha_S}. \quad (3)$$

A similar expression obtains for the anti-Stokes photon generation rate. Hence the ratio of Stokes-to-anti-Stokes scattering is

$$\frac{R_S}{R_{AS}} = \frac{\nu_S^3 \sigma_S(\nu_L, \nu_S) (\alpha_L + \alpha_{AS})}{\nu_{AS}^3 \sigma_{AS}(\nu_L, \nu_{AS}) (\alpha_L + \alpha_S)} \frac{(n + 1)}{n}. \quad (4)$$

Extraction of a phonon population  $n$  thus requires only knowledge of the frequency-dependent  $\sigma$  and  $\alpha$  factors in addition to the trivial  $\nu^3$  terms and a calibration of the throughput of the spectrometer system. Furthermore, assuming that a lattice temperature,  $T_L$  can be defined,  $n$  is given by the Planck distribution and  $(n + 1)/n = \exp(h\nu_0/kT_L)$ , where  $\nu_0$  is the phonon frequency. The  $\sigma$  and  $\alpha$  terms, however, are readily obtained by performing one additional Raman measurement at a new laser frequency  $\nu_{L'}$  chosen to be the same as the original anti-Stokes frequency  $\nu_{AS}$ . The ratio of the two Stokes rates is then formed,

$$\frac{R_S}{R_{S'}} = \frac{\nu_S^3 R_{L'} \sigma_S(\nu_L, \nu_S) (\alpha_{L'} + \alpha_{S'})}{\nu_{S'}^3 R_L \sigma_S(\nu_{L'}, \nu_{S'}) (\alpha_L + \alpha_S)}, \quad (5)$$

where, since  $\nu_{L'} = \nu_{AS}$  and  $\nu_{S'} = \nu_L$ , necessarily  $\alpha_{L'} + \alpha_{S'} = \alpha_{AS} + \alpha_L$ .

We now make use of the fact that the new Stokes cross section  $\sigma_S(\nu_{L'}, \nu_{S'})$  is identical to the original anti-Stokes cross section  $\sigma_{AS}(\nu_L, \nu_{AS})$  by time-reversal invariance. This is readily verified by reference to the diagrams of Fig. 1. (The time-reversal symmetry of the Raman cross section has been discussed by Loudon<sup>5</sup> and experimentally verified under strong resonance conditions by Compaan *et al.*<sup>6</sup>) Consequently, if the incident laser flux is held constant, the ratio of Eq. (4) gives exactly the product of correction factors required in Eq. (3) with no knowledge of lattice temperature required nor even that thermal equilibrium or steady-state conditions be present.

The application of the time-reversal invariance of the Raman cross section is crucial for analyzing Stokes-to-anti-Stokes ratios in semiconductors far from thermal equilibrium. We shall illustrate its use in the measurement of lattice temperatures in silicon during excitation by pulsed laser beams of energy density  $\sim 1 \text{ J/cm}^2$ . These are the conditions normally associated with pulsed laser annealing in Si.

We have used a double-beam system with a doubled Nd:YAG (neodymium-doped yttrium aluminum garnet) laser ( $\lambda = 532 \text{ nm}$ ) for excitation with a  $600\text{-}\mu\text{m}$  spot size at the  $0.4\text{-mm}$ -thick crystalline Si wafer and a  $N_2$ -laser-pumped dye laser, electronically delayed and operating at  $405 \text{ nm}$  to produce the Raman probe pulse.<sup>4</sup> The  $532\text{-}$  and  $405\text{-nm}$  pulse durations were  $10$  and  $7 \text{ ns}$  full width at half maximum, respectively. The  $405\text{-nm}$  beam was focused to a  $200\text{-}\mu\text{m}$ -diam spot at the center of the  $532\text{-nm}$  spot to minimize lateral temperature gradients. The  $405\text{-nm}$  wavelength was chosen to give a very short Raman probe depth  $1/(\alpha_L + \alpha_S) \sim 700 \text{ \AA}$  in room-temperature Si. (At higher temperatures the absorption increases still further.) Further details of the laser timing and data acquisition system are described in Ref. 4.

In order to obtain the correction factors for the Stokes-to-anti-Stokes ratio at  $405 \text{ nm}$  ( $\bar{\nu}_L = 24\,691 \text{ cm}^{-1}$ ) the laser frequency was shifted up by one phonon frequency ( $\Delta\bar{\nu} = 520 \text{ cm}^{-1}$ ) to  $\bar{\nu}_{L'} = 25\,211 \text{ cm}^{-1}$

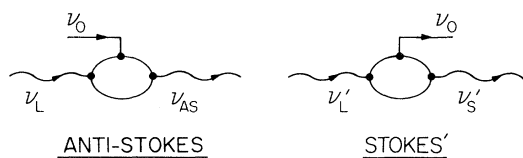


FIG. 1. Diagrams for the anti-Stokes Raman process with laser frequency  $\nu_L$  and the Stokes process with laser frequency  $\nu_{L'} = \nu_{AS}$ . The two cross sections are related by time-reversal invariance.

( $396.6 \text{ nm}$ ). The ratio of the two Stokes peaks corrected for the  $\nu^3$  factors and normalized to the same incident laser photon flux is shown as the quantity  $F$  in Fig. 2 where

$$F = \frac{(\alpha_{L'} + \alpha_{S'})}{(\alpha_L + \alpha_S)} \frac{\sigma_S(\nu_L, \nu_S)}{\sigma_{S'}(\nu_{L'}, \nu_{S'})}. \quad (6)$$

As a function of increasing  $532\text{-nm}$  excitation power, this factor shows a slight decrease which may be anticipated on the basis of the known spectral dependences of  $\alpha$  and  $\sigma$  at room temperature and the temperature shift of the band gap. Empirically the slopes of  $d\sigma/d\nu$  and  $d\alpha/d\nu$  are positive in the region near  $405 \text{ nm}$  ( $3.06 \text{ eV}$ )<sup>3,7</sup> since the frequency is approaching direct, allowed transitions ( $E_0'$  and  $E_1$  gaps) near  $365 \text{ nm}$  ( $3.4 \text{ eV}$ ). Inspection of Eqs. (4) and (6) then shows that although the increasing  $\alpha$  tends to suppress the anti-Stokes signal, the rising  $\sigma$  tends to enhance the anti-Stokes signal.<sup>8</sup> The corrections thus act in opposite directions and one expects  $F$  to be close to unity. However, as resonance is approached in most semiconductors, one typically<sup>9</sup> finds the slope  $d\sigma/d\nu$  to be larger than  $d\alpha/d\nu$  because  $\sigma$  involves the product of two electron-radiation field operators (one for virtual absorption, one for emission) whereas  $\alpha$  involves only one.<sup>5,9,10</sup>

In the case of Si under intense excitation, the temperature rise from the  $532\text{-nm}$  pulse is expected to heat the sample. Since the temperature shift  $dE_1/dT$  is negative, the direct gap will approach the Raman probe frequency and the product of correction factors  $F$  may be expected to decrease. Other effects due to high photogenerated carrier densities will no doubt also be present and this emphasizes the importance of an empirical measurement of these corrections. The usefulness of the time-reversal-symmetry argument is that it allows one to measure this correction factor directly and simply, and thus permits extrac-

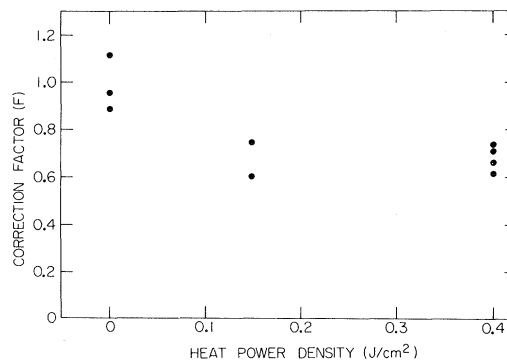


FIG. 2. The correction factor  $F$  (defined in the text), at a probe wavelength of  $405 \text{ nm}$  in Si, as a function of increasing heat-pulse power density at  $\lambda = 532 \text{ nm}$ . Probe pulse is delayed by  $30 \text{ nsec}$  from the heat pulse.

tion of an unambiguous phonon occupation factor from the Stokes-to-anti-Stokes ratio.

The temperature as inferred from the Stokes-to-anti-Stokes ratio with laser wavelength  $\lambda = 405$  nm is shown in Fig. 3 over the same range of pump powers as the correction factor shown in Fig. 2. In fact all conditions have been maintained constant for the two measurements. The only adjustments applied to the ratio, in addition to the factor  $F$ , are the  $\nu^3$  terms and corrections for instrumental throughput which were measured with a calibrated tungsten lamp. Note that the highest lattice temperature occurs at  $0.4 \text{ J/cm}^2$  of 532-nm power where the duration of the high-reflectivity phase is 20–30 nsec. When higher laser powers are used the duration of the high-reflectivity phase exceeds the 30-nsec-probe pulse delay and no Raman signal is observed. This confirms our earlier observation that the high-reflectivity phase is Raman silent.<sup>4</sup>

For 532 nm, energy densities of  $\sim 0.4 \text{ J/cm}^2$  are approximately sufficient to bring the silicon surface to the melting temperature if all the laser-deposited energy appears in the lattice and no diffusion occurs within roughly the pulse duration. The results of these Raman measurements appear to indicate that the silicon system is far from thermal equilibrium. Either the energy has diffused much further than expected or the energy remains trapped in the electronic system for a time much longer than expected on the basis of normal electron-lattice relaxation rates.

These results emphasize the unusual tool that

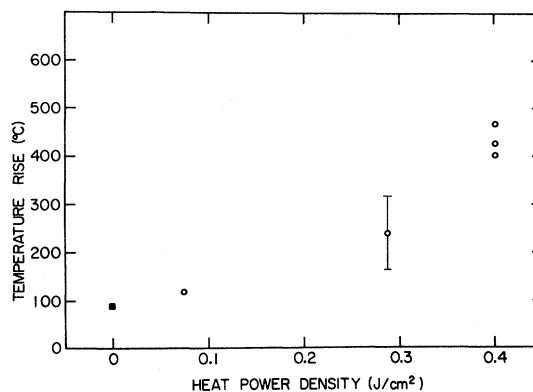


FIG. 3. Temperature rise as measured by Stokes-to-anti-Stokes ratios and for the same range of heat-pulse power densities as in Fig. 2. The appropriate correction factor  $F$  for the two intermediate powers has been interpolated from the data of Fig. 2.

time-reversal invariance affords the Raman scatterer who wishes to infer phonon occupation factors under nonequilibrium conditions and in situations where the spectral and temperature dependence of absorption and Raman cross section have not been independently measured.

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<sup>8</sup>R. F. Wood, M. Rasolt, and G. E. Jellison have used only the spectral dependence and an extrapolated temperature dependence of  $\alpha$  to argue that the temperature inferred from our Stokes-to-anti-Stokes data have not been sufficiently corrected for absorption effects [*Laser and Electron-Beam Processing of Materials*, edited by B. R. Appleton and G. Celler (Ref. 4), p. 61]. However, the experimental data of Fig. 2 and the discussion here show that the cross-section corrections are actually the larger effect. Furthermore, recent experimental results on the temperature dependence of  $\alpha$  for this region of Si show the earlier extrapolation of  $\alpha$  by Wood *et al.* to have been incorrect [G. E. Jellison, (private communication)].

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