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Importance of temperature-dependent optical properties for Raman-temperature measurements for silicon

G. E. Jellison, Jr., D. H. Lowndes, and R. F. Wood
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
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A standard relation of Raman scattering in the resonant regime is that the Raman matrix element R is well represented by $K\,d\epsilon/dE$, where ϵ is the dielectric function, E is the photon energy, and K is a constant. However, the only experimental check of this relationship in silicon [Renucci *et al.*, Phys. Rev. B 11, 3885 (1975)] concluded that it was only approximately valid. In this paper it is shown for silicon in the resonant regime that the agreement between the measured values of the Raman matrix element squared, $\sigma=|R|^2$ and $K^2|d\epsilon/dE|^2$, is very good indeed, if accurate values of the dielectric function are used. With the use of recently obtained temperature-dependent optical functions of silicon, the absorption coefficient, the Raman matrix element squared, the index of refraction, and the normal-incidence reflectivity are determined and shown to be strong functions of temperature in the resonant regime. The Stokes to anti-Stokes intensity ratio is calculated and found to compare favorably with values found in the literature for samples held at constant temperature. It is concluded that the temperature dependence of the optical properties must be included in any interpretation of measurements to determine the temperature from the Stokes to anti-Stokes intensity ratio.

I. INTRODUCTION

It is well known that the scattered light intensity in a Raman experiment is temperature dependent. The Raman interaction involves either the absorption (Stokes process) or emission (anti-Stokes process) of a phonon, and the population of phonons in the lattice at thermal equilibrium is given by

$$n_0(\omega_0,T)=[\exp(h\omega_0/kT)-1]^{-1}\,, \quad (1)$$

where ω_0 is the phonon frequency, T is the lattice temperature, and k is Boltzmann's constant. The ratio of the Stokes (S) to anti-Stokes (AS) intensities, R(S/AS), is often particularly sensitive to temperature and is therefore frequently used as a temperature probe. If the Stokes and anti-Stokes intensities depended *only* on the phonon population, then an expression of the form

$$R(\text{S/AS})=F(n_0+1)/n_0=F\exp(h\omega_0/kT)\,, \quad (2)$$

with $F=1$, would be valid. In practice, F can vary significantly from 1, and it depends upon such factors as probe wavelength, material, lattice temperature, lattice stress, and electron-hole—pair populations.

The first attempt to measure the temperature dependence of R(S/AS) in silicon was made by Hart *et al.*,[1] who examined the Raman scattering from the Γ'_{25} optical phonon utilizing a probe wavelength of $\lambda=514.5$ nm. More recently, Compaan and co-workers[2] and von der Linde and co-workers[3,4] measured the Stokes to anti-Stokes intensity ratio to determine the lattice temperature of silicon during and after pulsed laser annealing. The latter two groups concluded that the temperature never exceeds 450 °C, in contrast to the wealth of experimental and theoretical evidence showing that the lattice temperature during pulsed-laser annealing reaches and even surpasses the melting point of silicon (1410 °C).[5–11]

It is not the purpose of this paper to enter into the controversy concerning the results of these Raman-temperature measurements during pulsed-laser irradiation of silicon; this will be done in a planned future publication. Instead, we shall treat in detail the effects of constant lattice temperature on Raman scattering in silicon. That the prefactor F in Eq. (2) can be significantly different from 1 and can vary with temperature was pointed out by Wood and co-workers,[12] who showed that modest errors in F can lead to large errors in the lattice temperature determined from measurements of R(S/AS). We will show by direct calculation, using recent measurements of the optical properties of silicon as a function of temperature by Jellison and Modine,[13] that F *is* significantly different from 1 in certain wavelength (λ) regions and does vary with both temperature and probe wavelength.

II. THEORY

In a Raman scattering experiment the intensity of the S component is given by[14]

$$\frac{dI_S}{d\Omega}=K\omega_L\omega_S^3\frac{n_S(T)}{n_L(T)}\sigma_S(T)v_S(T)[n_0(\omega_0,T)+1]\,, \quad (3)$$

where the subscripts L and S identify the laser and Stokes wavelengths, respectively. The symbol n is the index of refraction, v is the effective volume, K is a constant, and σ is the Raman matrix element squared (sometimes referred to as the cross section). The anti-Stokes intensity can be obtained by substituting AS for S and n_0 for n_0+1 in Eq. (3). The results of Eq. (3) give the differential intensity per unit solid angle Ω *inside* the crystal. The total Stokes intensity *outside* the crystal can be determined in the backscattering geometry by integrating over the solid angle Ω; this is equivalent to replacing[14]

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$$K\frac{n_S(T)}{n_L(T)} \rightarrow K'\frac{[1-R_S(T)][1-R_L(T)]}{n_S(T)n_L(T)}, \quad (4)$$

where R is the reflectivity and $dI_S/d\Omega \rightarrow I_S$, in Eq. (3). If we now approximate the active scattering volume v_S by $[\alpha_S(T)+\alpha_L(T)]^{-1}$, where α is the absorption coefficient (this approximation is valid when $\alpha d \gg 1$, where d is the sample thickness[14]), we get

$$I_S = K'\omega_L\omega_S^3 \frac{\sigma_S(T)[1-R_S(T)][1-R_L(T)]}{n_S(T)n_L(T)[\alpha_L(T)+\alpha_S(T)]} \times [1+n_0(\omega_0,T)] . \quad (5)$$

With a similar expression for the AS component, R(S/AS) can be expressed as

$$R(\mathrm{S/AS}) = \left[\frac{\omega_S}{\omega_{AS}}\right]^3 \frac{t_S}{t_{AS}} \frac{\sigma_S(T)}{\sigma_{AS}(T)} \frac{\alpha_L(T)+\alpha_{AS}(T)}{\alpha_L(T)+\alpha_S(T)} \times \frac{n_{AS}(T)}{n_S(T)} \frac{1-R_S(T)}{1-R_{AS}(T)} \frac{n_0(\omega_0,T)+1}{n_0(\omega_0 T)} = \bar{\omega}\,\bar{t}\,\bar{\sigma}\,\bar{\alpha}\,\bar{n}\,\bar{R}\exp(h\omega_0/kT) = F\exp(h\omega_0/kT) . \quad (6)$$

In Eq. (6) we have included the spectrometer throughput correction $t_S/t_{AS}=\bar{t}$, which is a wavelength-dependent correction term dependent upon the experimental system. All newly introduced quantities are defined in an obvious way by the preceding terms of the equation.

III. CALCULATIONS

In Eq. (6), $\bar{\omega}$ and $\bar{t}$ can easily be measured, but the factors $\bar{\sigma}$, $\bar{\alpha}$, $\bar{n}$, and $\bar{R}$ require detailed knowledge of the temperature-dependent optical properties of Si which have only recently been measured over the extended temperature range from 10 to 972 K.[13,15,16] The most important correction factors are $\bar{\alpha}$ and $\bar{\sigma}$, but $\bar{R}$ and $\bar{n}$ can also be significantly different from 1. The temperature dependence of these correction factors, determined from the optical functions of Refs. 13, 15, and 16, is shown in Fig. 1 for probe wavlengths of 405 and 355 nm. The correction factors for $\lambda=532$ nm are independent of temperature up to $\sim$1000 K, and are given as follows: $\bar{\alpha}=1.198$, $\bar{\sigma}=0.908$, $\bar{R}=1.018$, and $\bar{n}=1.035$. As can be seen from Fig. 1, the correction factors are strong functions of both temperature and wavlength at $\lambda=355$ and 405 nm, because these wavelengths are near the room-temperature direct band gap of Si ($\sim$3.4 eV = 365 nm) and the direct band gap decreases as the temperature is increased (passing through 405 nm or 3.06 eV at 850 K).[16]

The temperature dependence of the absorption coefficient is particularly important, and is shown in Fig. 2 for $\lambda=355$, 397.6, 405, and 413.6 nm (the 397.6- and 413.6-nm wavelengths correspond to the Stokes and anti-Stokes components for a 405-nm probe beam). As can be seen, at low temperatures α increases exponentially with temperature for the 405-nm and associated lines but is nearly independent of temperature for the 355-nm line. At temperatures higher than $\sim$1000 K, α is expected to remain nearly constant for the 355-nm wavelength and to asymptotically approach saturation values of 7.2×10^5, 6.6×10^5,

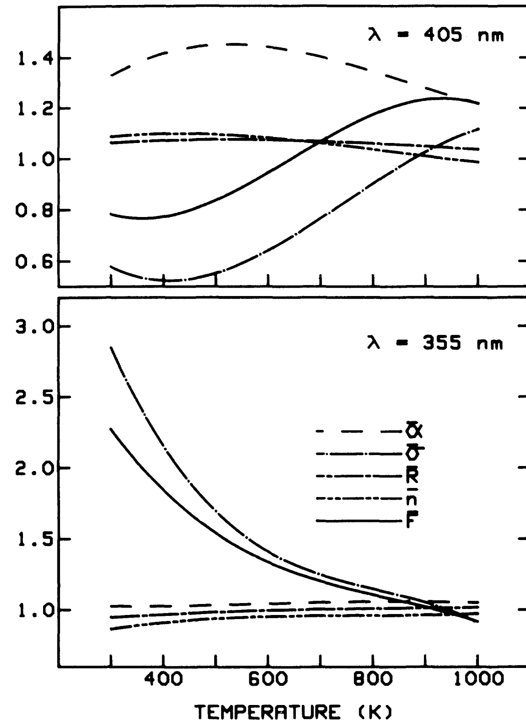

FIG. 1. Correction factor ratios $\bar{\alpha}$, $\bar{\sigma}$, $\bar{R}$, and $\bar{n}$ for the Stokes to anti-Stokes intensity ratio [Eq. (6)] vs temperature for the two probe wavelengths 405 and 355 nm.

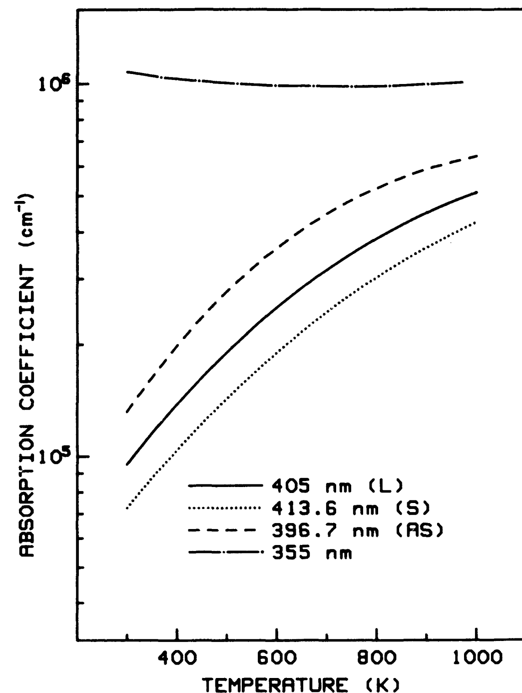

FIG. 2. Absorption coefficient α of silicon plotted vs temperature for the three wavelengths associated with Raman scattering at 405 nm. Also shown for reference is α at 355 nm.

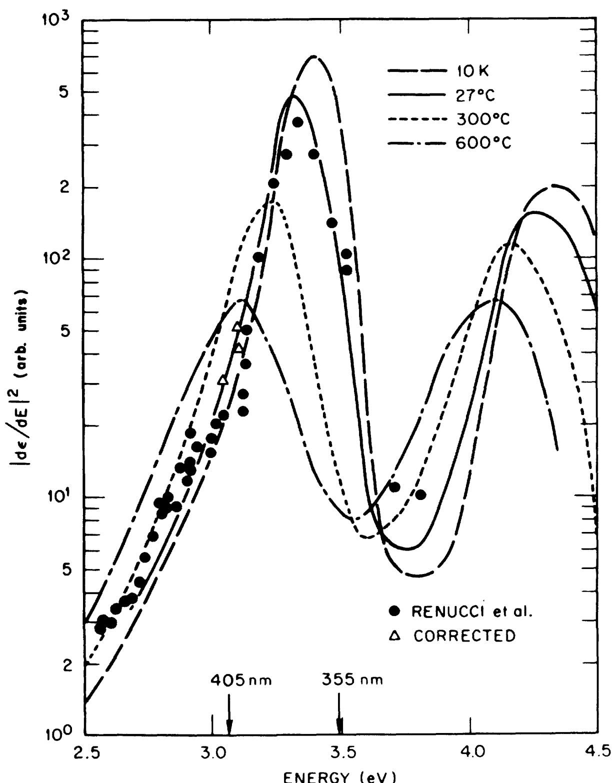

FIG. 3. Raman matrix element squared (determined in Ref. 17) compared with $|d\epsilon/dE|^2$ for several temperatures [determined by Eq. (7) using the optical data of Jellison and Modine (Refs. 13 and 15)]. The arrows at the bottom of the figure indicate the positions of the two probe wavelengths 405 and 355 nm, respectively. The data taken from Ref. 17 are shown by the closed circles (●), while the corrected values of the matrix element squared, determined from the data of Ref. 17 and the absorption coefficient data of Ref. 15, are shown by the triangles (△).

and 6.1×10^5 cm^{-1} for the anti-Stokes, laser, and Stokes wavelengths, respectively,[16] resulting in an asymptotic value $\bar{a}=1.1$ for the 405-nm probe wavelength.

The only measurements of σ for Si near the direct band gap were performed at 27 °C by Renucci *et al.*[17] and are shown by the data points (times an arbitrary constant) in Fig. 3. Theoretically, it is expected that[17]

$$\sigma(E,T)=CD\frac{\langle \xi^2(T)\rangle}{a^2}\left|\frac{d\epsilon}{dE}\right|^2 , \quad (7)$$

where C is a numerical factor, D is a linear combination of deformation potentials, ξ is the phonon amplitude $[\langle \xi^2(T)\rangle=\frac{1}{2}+n_0]$, a is the lattice constant, and ϵ is the complex dielectric function. Renucci *et al.* compared their data with calculations using Eq. (7) and the dielectric function determined from the reflectivity data of Philipp.[18] If the more accurate dielectric function determined from the scanning ellipsometry data of Jellison and Modine[13,15] is used in Eq. (7), a significantly improved fit to the data of Ref. 17 is obtained, as is shown by the curve for 27 °C in Fig. 3.

There appears to be a plateau in the data of Renucci *et al.* for σ near 405 nm (Fig. 3). (Compaan and coworkers[2] chose their probe wavelength at 405 nm just because of this plateau.) Renucci *et al.*[17] state that they used the α values of Philipp[18] and of Dash and Newman[19] in their determination of σ. However, it has been pointed out by Jellison and Modine[15] that the Dash and Newman[19] values of α used in Ref. 17 are much too low in the region near 405 nm. Because larger values of α result in higher values of σ, the plateau found by Renucci *et al.* is just an artifact of the α data used in the determination of σ. The corrected values of σ, determined from the data of Renucci *et al.* and the corrected values of α (from Ref. 15), are also given in Fig. 3 and show no evidence of a plateau in the 405-nm region.

Having confirmed that Eq. (7) gives a good functional representation of σ (E, 300 K), we calculated the curves for $|d\epsilon/dE|^2$ for several temperatures using the optical data of Jellison and Modine,[13,15] as shown in Fig. 3. From this figure and the close examination of the data on which it is based, the following features are clear: (1) As T increases, the low-energy peak in $|d\epsilon/dE|^2$ moves monotonically to lower energies and decreases exponentially in magnitude; (2) the minimum value of $|d\epsilon/dE|^2$ between the two peaks increases slightly in magnitude, while the valley moves monotonically to lower photon energies as T is increased; (3) near 405 nm, $|d\epsilon/dE|^2$ first increases and then decreases with increasing T; (4) near 355 nm, $|d\epsilon/dE|^2$ decreases rapidly with increasing temperature up to 200 °C, and then increases slowly with increasing temperature.

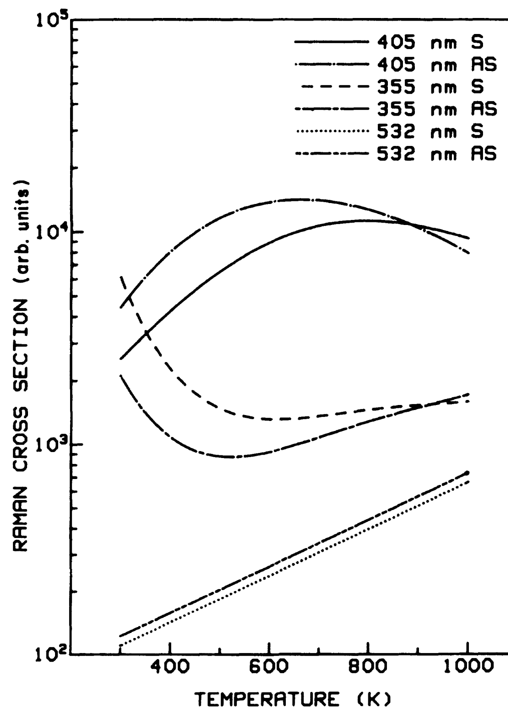

FIG. 4. Raman cross sections for the Stokes (S) and the anti-Stokes (AS) components plotted vs temperature for three different wavelengths. The cross sections were determined using Eq. (7) (405 and 355 nm) or Eq. (8) (532 nm) from the optical data of Refs. 13 and 15.

The temperature dependence of σ_S at 355 and 405 nm was determined using Eq. (7) and the calculated values of $|d\epsilon/dE|^2$. To determine σ_{AS}, we invoke the usual time-reversal argument,[14] which states that

$$\sigma_{AS}(\omega_L,\omega_{AS},T)=\sigma_S(\omega_{AS},\omega_L,T) ,$$

that is, σ_{AS} at ω_L is equal to σ_S at ω_{AS}. The quantities σ_S and σ_{AS} are shown in Fig. 4 for $\lambda=355$ and 405 nm, and the resulting correction factors are shown in Fig. 1.

For photon energies considerably below the direct band gap (such as 532 nm), the simple expression in Eq. 7 must be replaced by[20]

$$\sigma(E,T)=\frac{CD\langle\xi^2(T)\rangle}{a^2}\left|\frac{E}{E_d(T)}\frac{d\epsilon(E,T)}{dE}+\frac{1+\epsilon(E,T)}{E_d(T)}\right|^2 , \quad (8)$$

where $E_d(T)$ is the (temperature-dependent) direct band gap. Utilizing the temperature-dependent optical-function data of Jellison and Modine, one finds the empirical relations

$$\sigma_S=\sigma_S^0\exp(T/390) , \quad (9a)$$

$$\sigma_{AS}=1.10\sigma_S , \quad (9b)$$

and

$$\sigma_S(532\text{ nm},T=300\text{ K})=\sigma_S(405\text{ nm},\ T=300\text{ K})/23 , \quad (9c)$$

where T is in K. The derivatives taken in evaluating Eq. (8) are small at this wavelength, and the resulting error in σ can be as much as 25%. The quantities σ_S and σ_{AS} at 532 nm are also shown in Fig. 4.

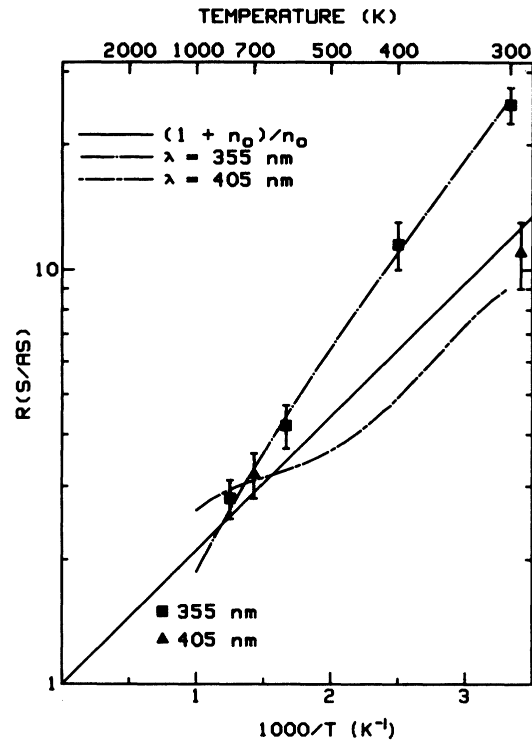

FIG. 5. Stokes to anti-Stokes intensity ratio for the zone-center optical phonon of silicon plotted semilogrithmically vs inverse temperature for probe wavelengths 355 and 405 nm. The solid line shows the value of R(S/AS) if no correction factors are involved and $R(\text{S/AS})=(1+n_0)/n_0$; this is very nearly the case for a probe wavelength of 532 nm ($F=0.97$). The actual measured values of R(S/AS) are shown by (a) solid squares (■), 355 nm (Ref. 4), and (b) solid triangles (▲), 405 nm (Ref. 2).

IV. DISCUSSION

From the values of the correction factors shown in Fig. 1, the R(S/AS) expected in Raman measurements on a sample held at constant temperatures may be calculated; Fig. 5 shows R(S/AS) for probe wavelengths of 355 and 405 nm. We have included the correction factors $\bar{\omega}$, $\bar{\alpha}$, $\bar{\sigma}$, $\bar{R}$, and $\bar{n}$ but not $\bar{t}$, since the spectrometer throughput factor is system dependent. The solid line shows the R(S/AS) expected if no correction factors are taken into account [$F=1$ in Eq. (2)]; since the total correction factor at 532 nm is 0.97 and is temperature independent (up to 1000 K), the calculated values for R(S/AS) for 532 nm are very close to this solid line.

The possible errors that may enter a Raman-temperature measurement by ignoring the temperature dependence of the F factor can now be examined. Assume that the sample is at 700 °C. According to Fig. 5, if the measuring wavelength is 405 nm, then a value for $R(\text{S/AS})=2.64$ should be expected; for 355 nm the measured R(S/AS) should be 1.87, while if $F=1$ is assumed, R(S/AS) would have the value 2.14. Conversely, if R(S/AS) is measured to be 2.64 utilizing $\lambda=405$ nm, the value for $T=700$ °C would be properly deduced from Fig. 5, but if it was assumed that $F=1$, a value of 447 °C would be deduced. Obviously, large errors can result from improper assumptions about the value of F. In particular, if determinations of the temperature are made with a probe wavelength of 405 nm and F is assumed to be 1, the temperature deduced will be significantly below the actual sample temperature for temperatures above 700 K. The plateau in R(S/AS) near $T=700$ K means that R(S/AS) is *not* sensitive to temperature in the range of sample temperatures from 600 to 1000 K, for $\lambda=405$ nm. For $T>1000$ K, the error appears to be even larger. Note also that errors in R(S/AS) will propagate to much larger errors in T at higher temperatures than at lower temperatures due to the functional form of Eq. (2).

Several measurements of the Stokes to anti-Stokes intensity ratio as a function of constant sample temperature can be found in the literature: (1) Hart *et al.*[1] at $\lambda=514.5$ nm using a cw argon ion laser and at temperatures up to 800 K, (2) von der Linde *et al.*[4] at $\lambda=355$ and 532 nm using a pulsed Nd:YAG (yttrium aluminum garnet) laser at temperatures from 300 to 800 K, and (3) Compaan *et al.*[2] at 405 nm using a nitrogen-pumped dye laser at $T=295$ and 700 K. In all of these measurements, sample heating by the probe laser may have been a problem. As silicon is heated, the absorption coefficient increases exponentially with temperature[16] for all photon energies less than the direct band gap (this excludes the measurement at only 355 nm); hence the volume in which the probe beam is ab-

sorbed decreases exponentially with temperature; therefore, probe-beam heating can become significant at elevated temperatures, even if no probe-beam heating is observed at room temperature.

Since 514.5 nm is well below the direct band gap, $F \sim 1$ and is independent of temperature; therefore, $R(S/AS)$ is given by the solid line in Fig. 5. However, Hart *et al.*[1] observed Stokes to anti-Stokes intensity ratios that were consistently below the values of $R(S/AS)$ calculated from Eq. (2) with $F=1$, which correspond to higher sample temperatures. Since they used a 200 W/cm^2 probe beam, it is likely that they were heating the sample. In particular, they observed a larger discrepancy between the observed and calculated $R(S/AS)$ at higher temperatures than at room temperature; this is entirely consistent with the above observation relating to the increased heating by the probe beam at higher temperatures.

The 355-nm pulsed Raman constant-temperature measurements of von der Linde *et al.*[4] agree very well with our $R(S/AS)$ determined from the optical properties (see Fig. 5). The values of $R(S/AS)$ measured by von der Linde *et al.*[4] at 532 nm indicate that $F \simeq 0.6$ and is temperature independent, while the optical properties predict that $F \cong 1$. This discrepancy was noted by von der Linde *et al.*[4] and was ascribed to the spectrometer throughput factor ($\bar{t}$). With this factor taken into account, the measured $R(S/AS)$ and the $R(S/AS)$ calculated from optical properties measurements are in agreement at 532 nm.

Measurements of $R(S/AS)$ at 405 nm at constant temperatures have been made by Compaan *et al.*[2] at two temperatures: 295 and 700 K; their experimental values of $R(S/AS)$ agree with our calculated results, as can be seen from Fig. 5.

To summarize, we have shown that the Raman matrix element squared is very well represented by Eq. (7), if accurate optical data is used. All of the correction factors that enter into a Stokes to anti-Stokes Raman-temperature measurement can be calculated from the temperature-dependent optical properties, as can the Stokes to anti-Stokes intensity ratio itself. The calculated values of $R(S/AS)$ have been shown to agree very well with constant-temperature Raman measurements of $R(S/AS)$ found in the literature. Therefore, these correction factors must be included in any Raman-temperature measurement. Since it is possible that $R(S/AS)$ may be very insensitive to temperature for certain values of probe wavelength and/or temperature (such as a probe wavelength of 405 nm and a temperature between 600 and 1000 K), extreme caution must be employed in determining temperature by measurements of $R(S/AS)$.

In conclusion, we note that no mention has been made in this paper of Raman-temperature measurements during pulsed-laser annealing of silicon. In that case several additional factors enter into and further complicate the determination of the Stokes to anti-Stokes intensity ratio, including stress effects and the existence of excess electron-hole pairs. These factors will be the subject of a subsequent paper.

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