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INTERACTION BETWEEN ELECTRONIC AND VIBRONIC RAMAN SCATTERING IN HEAVILY DOPED SILICON

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The asymmetry in the one-phonon Raman lines of heavily doped *p*-type Si is interpreted as the interference of a continuum of electronic excitations with the phonon line. The dependence of the line shape on the exciting frequency is produced by the different resonant behavior of these two scattering mechanisms.

HEAVY acceptor doping is known to affect the position and width of the one-phonon Raman lines of Ge and Si.[1] In contrast to Ge, the broadening produced by this doping in Si is asymmetric[1] and depends on the frequency of the scattering light.[2] In this letter we propose that this effect is the result of a discrete-continuum, Fano-type[3] interaction between the phonon scattering and one electron excitations from filled to empty valence states. The dependence on on scattering frequency of the observed line shapes arises then naturally as a result of differences in the energy denominators for the electronic and one phonon Raman scattering. The puzzling observation of Beserman *et al.*[2] that the shift in the phonon frequency induced by the carrier concentration decreases as the wavelength of the scattering radiation increases can be easily explained with our mechanism: because of the asymmetry of the Fano-line-shape, its maximum does not correspond to the critical energy. Once the critical energies are extracted from a fit of the experimental line shape with Fano's theory,[3] the critical frequencies are found to be independent of the scattering light wavelength and to decrease monotonically with doping.[4]

The measurements reported here were performed at room temperature on boron-doped Si,[5] polished with Al_2O_3 and etched with CP4. The back-scattering configuration with a conventional double monochromator and detection by photon counting was used. Measurements were performed with several lines of *A*-ion (4545, 4880, 5145 Å) and Kr-ion (5682, 6471 Å) lasers.

The line shapes obtained for a sample with $p = 1.6 \times 10^{20}$ cm^{-3} at different scattering wavelengths are shown in Fig. 1 (discrete points). They were fitted with Fano's expression (solid lines) for the interaction of a discrete scattering state (phonon) with a continuous background (electronic excitations between valence bands, to be discussed later) given by:

$$I = \frac{(q+\epsilon)^2}{1+\epsilon^2}$$
$$\epsilon = (\omega - \Omega)/\Gamma, \qquad (1)$$

where ω is the measured frequency, Ω is the critical frequency (dressed one-phonon excitation) and q and Γ (defined in reference 3) were used as curve-fitting parameters. The fit obtained (Fig. 1) is in all cases excellent and, in particular, reproduces well the antiresonance observed at low wave numbers for high exciting wavelengths (5682, 6471 Å). The values obtained for the fitting parameters and critical frequency are listed in Table 1. The following observations can be made:

1. All curves in Fig. 1 can be fitted with the same value of Γ ($\Gamma = 8.24$ cm^{-1}), in accordance with Fano's interpretation of this parameter as the squared matrix element of the coupling between the continuum and the discrete state:[3] such coupling should have no relationship with the scattering wavelength.

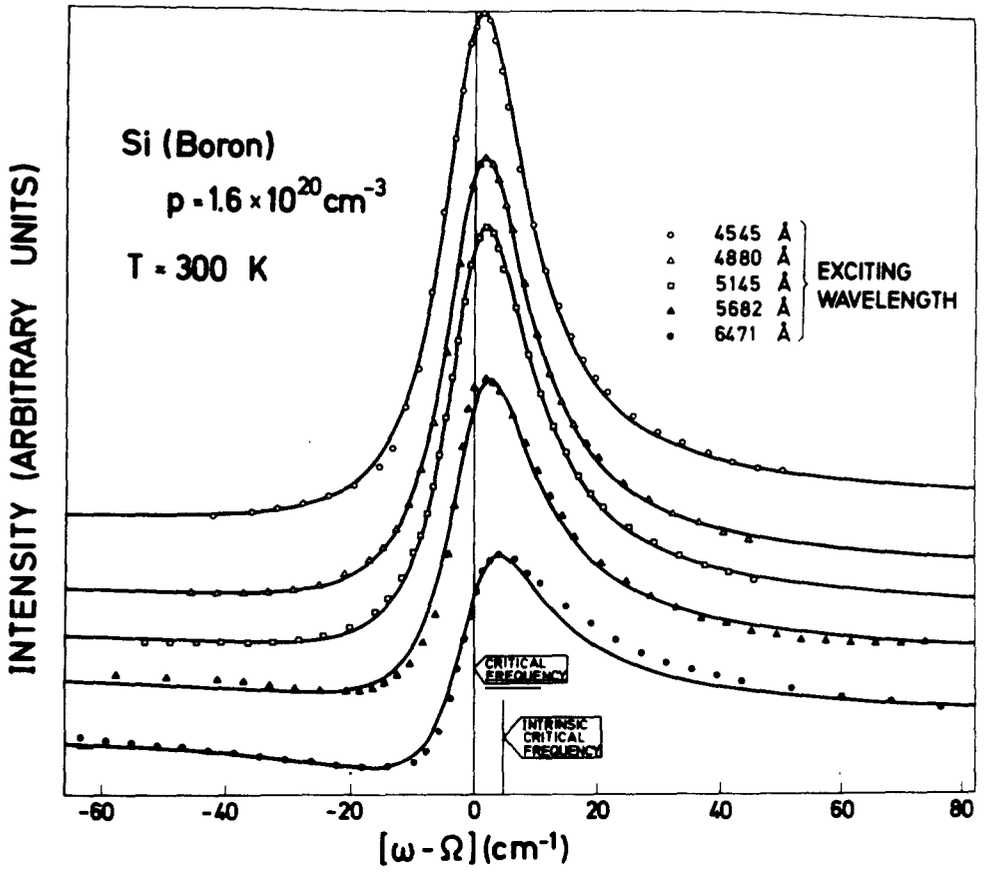

FIG. 1. Raman lineshapes vs scattering wavelength for p-Si. The solid lines are theoretical fits, with equation (1), to the experimental lines (discrete points). The curves have been shifted vertically with respect to each other, with the antiresonance minimum in each case defining the base line. The critical energy is the same for all curves. The relative heights of the different curves are the ones found experimentally.

Table 1. Parameters obtained from the fitting of the experimental data with the curve of equation (1). Here $\delta\Omega_m$ *and* $\delta\Omega$ *are the peak position and critical frequency respectively, measured from the position of the intrinsic peak* ($\delta\Omega_m = \Omega_m - \Omega_{intrinsic}$, $\delta\Omega = \Omega - \Omega_{intrinsic}$). *The value of* Γ *is the same in all cases,* $\Gamma = 8.24\ cm^{-1}$

Scattering wavelength (Å)	q	$\delta\Omega_m(cm^{-1})$	$\delta\Omega(cm^{-1})$
4545	7.0	−3.6	−4.8
4880	5.1	−3.3	−4.9
5145	4.2	−2.5	−4.4
5682	3.2	−2.9	−5.4
6471	2.0	−0.8	−4.9

2. The square of the parameter q, however, represents the ratio of the scattering probability of the discrete state to that of the continuum. Hence q can exhibit a dependence on the frequency of the scattering light if the two processes have different frequency dependences. Table 1 shows indeed a strong increase in q with increasing photon energy.

The insertion in Fig. 2 shows the band diagram of heavily doped p-type Si around k = 0. Electrons can be excited from the two lower valence bands to the empty states of the upper ones. In this manner a continuum of excitations arises which overlaps the phonon frequency (0.065 eV) for $p > 2 \times 10^{18}\ cm^{-3}$. These excitations are infrared forbidden[6] but Raman allowed at k = 0 because of parity. The expression for the leading term near resonance of the $\Gamma_{25'}$ Raman tensor component for this electronic scattering

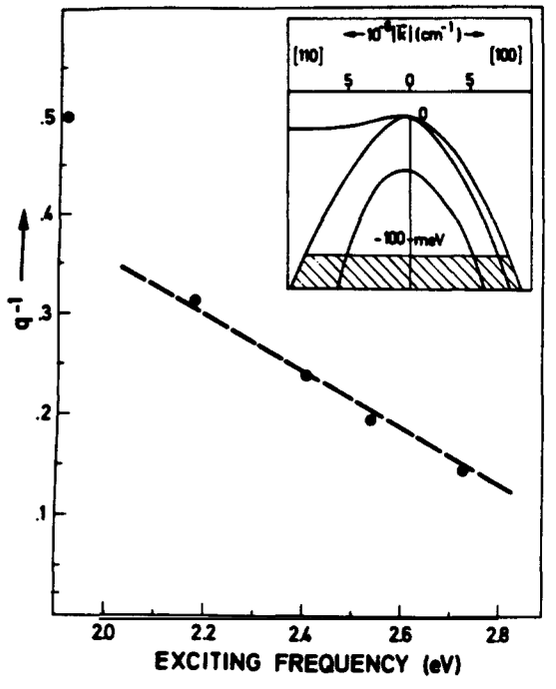

FIG. 2. Plot of q^{-1} vs exciting frequency as obtained from the lineshape fitting in Fig. 1 (discrete points). The dashed line was computed with the resonance expression described in the text. The insert shows a detail of the valence band in Si along two directions in the B.Z., with the Fermi level for 1.6×10^{20} holes/cm^3 indicated.

mechanism is,[7]

$$R_e \propto \sum_i \frac{\langle f|p_y|i\rangle\langle i|p_x|0\rangle}{(\omega_f - \omega_i) - \omega_L}, \qquad (2)$$

where $|0\rangle$ and $|f\rangle$ represent the initial and final states respectively, ω_L is the frequency of the scattering radiation and **p** is the linear momentum. We have assumed that the scattering frequency of the electronic excitation is small compared with the energy denominators of equation (2). The leading term in the Raman tensor for one-phonon scattering is:[8]

$$R_p \propto \sum_i \frac{\langle 0|p_x|i\rangle\langle i|p_x|0\rangle}{[(\omega_f - \omega_i) - \omega_L]^2}. \qquad (3)$$

Equation (3) resonates for ω_L approaching the energy gap of the material more rapidly than equation (2), a fact which explains the increase in $q \propto |R_p/R_e|$ with increasing scattering frequency found experimentally. The electronic excitation spectrum of silicon can be approximated as a one-dimensional critical point E_0' at 3.3 eV plus another one E_2 at 4.3 eV. In the case of a one-dimensional critical point of frequency ω_0 equation (2) reduces to $R_e \propto (\omega_0 - \omega_L)^{-1/2}$ and equation (3) to $(\omega_0 - \omega_L)^{-3/2}$ for $\omega_L \simeq \omega_0$. Thus, in this case, we find:

$$q^{-1} \propto (\omega_0 - \omega_L). \qquad (4)$$

Equation (4) is represented by the dashed line of Fig. 2 for $\omega_0 = 3.3$ eV.[9] Admixing E_2 to the E_0' scattering mechanism only reduces the agreement between experiment and theory. However, the fit of the resonance expressions to the experimental points should be regarded as a semiquantitative comparison, since those expressions are only valid in the immediate neighbourhood of the resonant gap. The present comparison shows that the frequency dependence found for q has the right tendency.

The experimental data (see Fig. 1) show an apparent dependence of the peak position on the exciting frequency. This was also observed by Beserman *et al.*[2] In the context of the present interpretation, however, the relevant quantity giving the energy of the scattering phonon (Ω) is *not* the position of the maximum (Ω_m) but the critical energy in equation (1) related to Ω_m by

$$\Omega = \Omega_m - \Gamma/q, \qquad (5)$$

a quantity that in contrast to Ω_m, should be clearly independent of the exciting frequency. Indeed the values found for Ω from our curve-fitting (see Table 1) show no systematic dependence on exciting frequency but scatter around a value which is 4.9 cm^{-1} below the intrinsic frequency [$\delta\Omega = \Omega - \Omega_{\text{intrinsic}} = -4.9$ cm^{-1}]. This is further evidence of the self-consistency of our interpretation. The fact that Ω lies below the corresponding value for the intrinsic material is a result of the change in phonon self-energy due to the electron–phonon interaction in a way similar to that discussed in references 1 and 10.

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Die beobachtete Asymmetrie der 1-Phonon Ramanlinien in stark dotiertem *p*-Typ Si wird als Interferenz eines Kontinuums elektronischer Anregungen mit dem diskreten Phononzustand interpretiert. Die Aenderung der Linienform mit Laserfrequenz rührt von den verschiedenen Mechanismen und Frequenzabhängigkeiten der elektrischen und vibronischen Streuung her.