RAMAN SCATTERING FROM DONOR AND ACCEPTOR IMPURITIES IN SILICON

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We report the observation of electronic Raman scattering from phosphorus donors and boron acceptor impurities in silicon. We find that the most important intermediate states involve interband transitions, and that this has important consequences for the intensity of the scattering. We also report observation of phonon-Raman scattering involving creation of one zone-center optical phonon with subsequent decay through the anharmonic interaction into two acoustic phonons.

Raman spectroscopy is a useful tool for studying electronic transitions which may be forbidden by one-photon selection rules, or which occur in an inconvenient spectral region for infrared spectroscopy. Electronic Raman scattering involving impurities was first proposed by Elliott and Loudon,[1] and subsequently observed by Hougen and Singh[2] in $PrCl_3$. Subsequent observations have been made on rare-earth atoms[3] and shallow acceptors in GaP.[4] In the present work, performed on oriented single crystals, we have been able to demonstrate the symmetry of the Raman-scattering tensor, and to obtain spectra free from luminescence and from broadening effects due to overlap of impurity wave functions. The theory for shallow donor states[5] is sufficiently well developed to allow estimates of the scattering cross section, and to demonstrate the disappearance of some transitions allowed by symmetry.

Experiment.—The Raman spectra were excited by a 1-W cw neodymium-doped yttrium aluminum garnet laser operating at 1.0648 μ, and recorded at 90° with a SPEX model 1400 double-grating monochromator and a cooled $S1$ photomultiplier. The samples were conduction cooled in a liquid-helium Dewar. The samples were transparent to the laser at helium temperature, but showed both absorption and luminescence at nitrogen temperature. We ran photoluminescence spectra, pumped with a high-pressure mercury arc lamp, and observed the bound-exciton spectra reported by Haynes,[6] but none of the lines coincided with the observed Raman lines. The unpolarized helium-temperature Raman spectrum for a sample containing 1.6×10^{16} cm^{-3} phosphorus donors is shown in Fig. 1(a). The single sharp line at 13.1 meV is the electronic Raman transition, and was shown by polarized-light experiments to have a diagonal scattering tensor. The zone-center optical phonon at 64.8 meV shows the polarization tensor expected[7] for a $\Gamma_{25'}$ phonon, as does the line at 37.9 meV. This last line also occurs in high-purity silicon. The Raman spectrum for a sample containing 1.2×10^{16} cm^{-3} boron acceptor impurities is shown in Fig. 1(b). The phonon lines at 64.8 and 37.9 meV recur, and in addition there is an electronic Raman line at 23.4 meV which shows the same polarization symmetry as the main phonon line. Choosing appropriate polarizations, and correcting for the spectral response of the equipment, we measured the ratio of the scattering strength of the weaker processes to that of the main phonon line. The result was 16×10^{-4} for 1.6×10^{16} cm^{-3} phosphorus donors, 14×10^{-4} for 1.2×10^{16} cm^{-3} boron acceptors, and 6×10^{-4} for the phonon line at 37.8 meV.

Discussion: (a) Donors.—Some of the energy levels for phosphorus donor impurities in silicon are shown in Fig. 2(a), with labels indicating the single-valley effective-mass envelope function and symmetry type corresponding to the T_d site symmetry. The arrow indicates the electronic Raman transition we have observed. Raman transitions to both the $1S(E)$ and $1S(T_2)$ states are allowed by symmetry, but using the wave

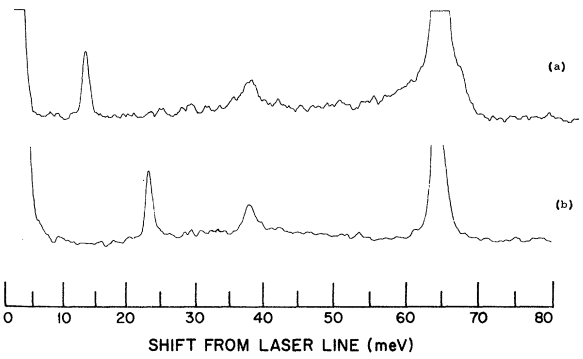

FIG. 1. Raman spectra of impurities in silicon at 4.2°K; (a) phosphorus donors, $n = 1.6\times10^{16}$ cm^{-3}, and (b) boron acceptors, $p = 1.2\times10^{16}$ cm^{-3}.

functions given by Kohn,[5] it is possible to show that the strength of the $1S(T_2)$ transition vanishes except for admixture of higher states. The strength of the one-photon infrared-allowed transition $1S(A_1) \rightarrow 1S(T_2)$ also vanishes except for admixture of higher $P(T_2)$ states by the nonspherical part of the impurity potential. The energy of the $1S(T_2)$ and $1S(E)$ states has been precisely established by Aggarwal and Ramdas[8] in a clever experiment involving thermal population of the upper levels.

Using the approach of Elliott and Loudon,[1] we may express the scattering efficiency S per unit path length L and solid angle Ω due to the interband terms in terms of the transverse effective mass $m_\perp{}^*$, and the energies $E_1 = 4.43$ and $E_2 = 3.36$ of the Δ_5 bands above and below the conduction band. For an impurity concentration N/V, we obtain

$$\frac{S}{L\Omega} = \frac{N}{V}\left(\frac{e^2}{mc^2}\right)^2\left(\frac{\omega_R}{\omega_L}\right)\left[\left(\frac{m}{m_\perp{}^*}-1\right)\frac{E_1E_2}{(E_1-E_2)}\left(\frac{E_1}{E_1{}^2-\hbar\omega_L{}^2}-\frac{E_2}{E_2{}^2-\hbar\omega_2{}^2}\right)\sum_j \alpha_j(f)\alpha_j(0)\langle F_{fj}|F_{oj}\rangle\right]^2, \quad (1)$$

where o and f refer to initial and intermediate states, L and R refer to laser and Raman photons, F_{fj} is the effective-mass envelope function for the fth state of the jth valley, and α_j is the coefficient necessary to combine the single-valley functions with the correct symmetry.[5] The sum over j includes only those valleys for which the electric vector of the radiation is transverse to the valley. For intraband contributions, the sum within the brackets may be shown[9] to be approximately $(m/2m_\perp{}^*) \times (E_B/\hbar\omega_L)^2$ which for phosphorus in silicon is about 5×10^{-3}. With $N/V = 1.6\times10^{16}$ cm^{-3}, $\hbar\omega_L = 1.165$ eV, and $m/m_\perp{}^* = 5$, we find $S/L\Omega = 6\times10^{-9}$ for the interband contribution. This would imply that $S/L\Omega$ for the main phonon line is about 10^{-6}, in agreement with estimates by Loudon.[7] Unfortunately, it is very difficult to obtain a reliable measurement of the absolute cross section, especially at helium temperature. In the effective mass approximation, the projection of F_{oj} on F_{fj} vanishes unless the final state is derived from a 1S state. This explains the dominance of the transition we observe over transitions to states such as $2S(E)$. The transition to $1S(T_2)$ disappears because of the vanishing of the sum over the α_j's for this state.[5]

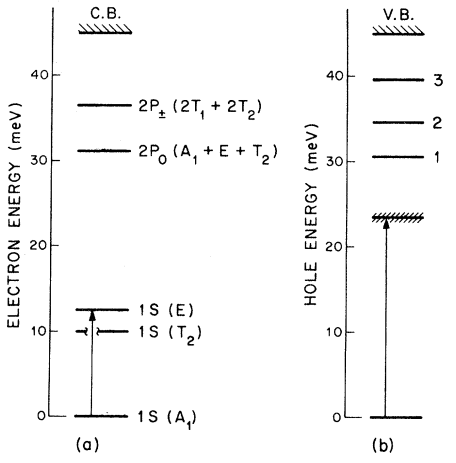

FIG. 2. Energy levels of (a) phosphorus donors and (b) boron acceptors in silicon. Arrows show the electronic Raman transitions observed. Labels of the states are those of Ref. 8 for phosphorus and Ref. 10 for boron.

(b) Acceptors.—The single strong transition we observe in boron-doped silicon is shown on an energy diagram in Fig. 2(b) at 23 meV, well below any of the transitions observed in infrared absorption.[10] The numerical labeling of the states reflects the fact that the spectrum is nonhydrogenic. No theoretical energy calculations have been published for states which are not infrared allowed, so we may only speculate as to its nature. Reasoning similar to that followed in treatment of the donors leads us to believe that interband terms are again dominant. In this case, the relevant levels are the Γ_{15} at 2.5 eV, and the Γ_2 at 4.1 eV.[11] We can again calculate the matrix components of momentum from the hole effective masses, but now we do not know the projection of the final-state envelope function upon the initial state. We do know, however, that for interband intermediate states we can only reach a final impurity state with the same parity as the ground state. This is why the state is not observable by one-photon infrared spectroscopy. The fact that we observe only one state, even with $N = 2\times10^{17}$ cm^{-3}, will be an impor-

tant point to explain when new impurity calculations are made. We observe none of the broadening which Henry, Hopfield, and Luther[4] attributed to phonon coupling in GaP, but this is not surprising, in that silicon is neither piezoelectric nor polar. Our highest concentration was still an order of magnitude lower than the GaP experiments, and it is possible that broadening and breakdown of selection rules will begin to occur with overlap.

(c) One-phonon anharmonic decay.—The line we observe at 37.9 meV has been predicted by Cowley,[12] and arises from a peak in the inverse lifetime of the zone-center optical phonon. The chief contribution to the inverse lifetime of this phonon comes from decay through the anharmonic interaction into two acoustic phonons. Energy conservation for the process is made possible only by the presence of the laser light, hence we speak of "pumped decay." The line we observe corresponds to a peak in the phonon density of states for the transverse acoustic branch. As the electronic process proceeds through a virtual zone-center optical phonon, the scattering tensor has the same symmetry as that for the main phonon line. Other anharmonic processes are expected to contribute, including a similar decay through the longitudinal acoustic branch, and this likely accounts for the asymmetry of the main phonon line, exhibited clearly in Fig. 1(a). Using a shell model for the phonons, Cowley[12] calculated a ratio of 5×10^{-3} at 300°K for the strength of the 38-meV line compared with the main phonon line. At 4°K the relative strength decreases to about 2×10^{-3}, which is better agreement with experiment than is to be expected considering the possible calculational and experimental error.

In summary, we have observed electronic Raman scattering due to donor and acceptor impurities in silicon. We have shown that the important intermediate states involve interband transitions, and that as a consequence, the strongest Raman transitions will be between initial and final states having a strong overlap between their "single-valley envelope functions." In the case of the donor, the transition $1S(A_1) \rightarrow 1S(E)$ completely dominates all other transitions. In boron-doped silicon we observe a new excited state of the acceptor, below the states previously observed in infrared absorption. Finally, we report the observation of pumped one-phonon decay due to anharmonic forces, predicted by Cowley.

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