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Vibrational spectroscopy of acceptor-hydrogen complexes in silicon: Evidence for low-frequency excitations

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The infrared spectra of acceptor-H centers in passivated Si for B, Al, and Ga provide evidence for an unexpected low-frequency excitation of the complexes. The broad vibrational bands observed near 2000 cm^{-1} at room temperature shift to higher frequency and narrow dramatically upon cooling to He temperature. While the B-H–related band remains structureless at intermediate temperatures, the vibrational bands observed for Al-H and Ga-H complexes show thermally populated sidebands to the low-energy side of the main vibrational bands. The sidebands indicate the presence of a low-frequency excitation of the complex. We have determined Boltzmann energies of 78 and 56 cm^{-1} from the intensity of the sidebands as a function of temperature for Al-H and Al-D complexes, respectively. The absence of an anomalously large isotope shift is consistent with this excitation being due to an ordinary vibration rather than a tunneling splitting as is sometimes observed for hydrogen-containing complexes.

I. INTRODUCTION

Both deep and shallow levels in semiconductors can have their electrical characteristics modified by atomic hydrogen that is introduced intentionally or accidentally by, for example, exposure to a H_2 plasma, polishing, or boiling in water.[1] The mechanism for the hydrogen-passivation effect and the structures of the complexes that might form are controversial.[2–10] Of the various defects studied, group-III-acceptor–H complexes in Si are among the simplest. Thus we investigate this system in detail.

Pankove *et al.*[4] and Johnson[10] have reported a vibrational band near 1875 cm^{-1} for the B-H complex in Si at room temperature. A similar band is also seen in the Raman spectrum of passivated B-doped Si.[11] Pankove and co-workers[4] proposed a structural model in which the H is in an interstitial configuration along the $\langle 111 \rangle$ axis between the B acceptor and one of its Si neighbors with the H bonded primarily to the Si because the observed vibrational frequency is closer to typical Si-H frequencies than to B-H frequencies in other systems. DeLeo and Fowler[5,6] have done cluster calculations that support Pankove's model[4] and reproduce the observed frequency for the B-H complex. These authors also predict a vibrational frequency of 2220 cm^{-1} for the Al-H complex.[6] For the model of Pankove *et al.* these $\sim$2000-cm^{-1} vibrations are primarily longitudinal Si—H stretching vibrations. Assali and Leite[7] have performed cluster calculations and propose an alternative model. The most stable configuration of the acceptor-H complex was found to be one with the H along the $\langle 111 \rangle$ axis between the acceptor and the tetrahedral interstitial site.

We have recently measured the vibrational frequencies near 2000 cm^{-1} for acceptor-H complexes for B, Al, and Ga acceptors.[12] We obtained good agreement with the prediction made by DeLeo and Fowler[6] for Al-H. Recent channeling results[13–15] also provide direct support of the $\langle 111 \rangle$ configuration with H bonded to Si suggested by Pankove *et al.*[4]

We noted in our previous work[12] that there was a pronounced narrowing and a shift to higher frequency for the $\sim$2000-cm^{-1} vibrations of the acceptor-H complexes upon cooling to low temperature. For Al-H and Ga-H complexes a sideband to the main vibrational band was observed that indicates that there is a low-frequency excitation of the complex. Here we will present more detailed observations of these sidebands and the vibrational line shape as a function of temperature. From the temperature dependence of the sideband intensity we determine the energy of the low-frequency excitation.

In complexes that contain hydrogen it has been reported that the hydrogen can tunnel between equivalent sites.[16–19] Muro and Sievers[19] have observed directly the tunneling splittings for Be-H and Be-D complexes in Si by far-infrared spectroscopy. There was a giant isotope shift of the tunneling splitting upon substituting D for H [i.e., much greater than $(M_D/M_H)^{1/2}$, where M_H and M_D are the masses of hydrogen and deuterium, respectively] that was taken to be strong evidence for the tunneling hypothesis for the Be-H (-D) complexes. Here, we will determine the isotope shift for the low-energy excitation associated with the Al-H (-D) complex. For Al-H (-D) we will find no giant isotope shift and therefore no evidence for tunneling in the group-III-acceptor–H complexes.

We find that our vibrational line shapes are broad ($\sim$10 cm^{-1}) and asymmetric even at low temperature. Our samples consist of partially passivated layers of acceptors that were implanted to high concentration. We suggest that the broad linewidth is due to the combined effects of implant-related damage and a Fano-resonance interaction between the Si-H vibration and the residual free-carrier continuum.

II. EXPERIMENTAL PROCEDURE

The diffusion depth of hydrogen is only a few micrometers for diffusion times of a few hours at temperatures where acceptor-H complexes are stable. To obtain the number of centers required for ir-absorption measurements in thin, near-surface layers, Si wafers were implanted with B, Al, or Ga at energies of 30, 100, and 180 keV to a total fluence of $2\times10^{15}-10^{16}$ cm^{-2}. The implants were activated with a rapid thermal-annealing treatment of 1200 °C for 60 s. Portions of each wafer were exposed to an H_2 or D_2 plasma in a Technics Planar Etch II parallel-plate reactor operating at 30 kHz, with a power density of <0.08 W cm^{-2}, and with a pressure of 750 mTorr. Exposure was 3 h for each side of the wafer at 120 °C for the B implant, 180 °C for the Ga implant, and 220 °C for the Al implant. The passivation temperatures were chosen to be near the maximum temperature for acceptor-H pair stability (see Fig. 1) for the different acceptors to optimize the diffusion depth of the hydrogen or deuterium.

Spreading resistance and free-carrier absorption were used to characterize the implanted wafers before and after the hydrogen- or deuterium-passivation treatments. Typical spreading-resistance profiles for the Al and Ga implants have been reported elsewhere.[12] The B, Al, and Ga implants gave doped layers approximately 1.5, 1.2, and 0.4 μm thick with peak concentrations of 3×10^{19}, 3×10^{18}, and 10^{19} cm^{-3}, respectively. Our hydrogenation treatments passivated about 90% of the Al acceptors, about 80% of the Ga, and about 75% of the B. For all the acceptors the passivation treatment decreased the free-carrier absorption dramatically.

ir-absorption measurements were made with a Nicolet 60SX Fourier-transform spectrometer at a resolution of 2 or 4 cm^{-1}. Samples were cooled with an Air Products Helitran cryostat.

In addition to the infrared-absorption features that will be described here, our plasma treatments often gave rise to broad features in the infrared-absorption spectra that were measurement-temperature independent and showed no isotope shift or acceptor dependence. These features, which we attribute to surface damage or contamination, could be removed by a mild etching treatment which consisted of sequentially rinsing the sample with HNO_3, HF, and H_2O. The acceptor-H absorption features remained following this mild etch.

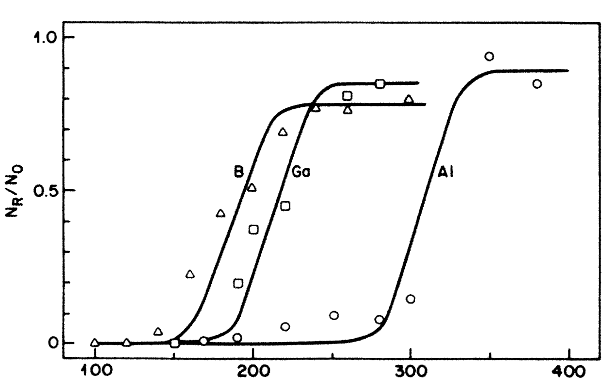

FIG. 1. The thermal-annealing recovery of the electrical activity of hydrogen-passivated shallow acceptors. The recovered fraction, N_R/N_0, following annealing for 5 min at the temperature shown was determined from spreading-resistance profiles of bulk p-type silicon. The lines shown are to guide the eye.

III. VIBRATIONAL SPECTRA FOR ACCEPTOR-H COMPLEXES

Spectra are shown in Figs. 2(a) and 2(b) for B-H and B-D complexes at several temperatures. At room temperature the frequencies and linewidths are in good agreement with previously reported results.[4,11] Upon cooling, the vibrational bands narrow and shift to higher frequencies. At He temperature the frequencies are 1903 and 1390 cm^{-1} and the full widths at half maximum (FWHM) are 9 and 7.5 cm^{-1} for the B-H and B-D complexes, respectively. At intermediate temperatures there is no additional structure observed that might explain the frequency shift upon cooling. The vibrational bands also remain rather broad and are asymmetric at the lowest temperature.

Spectra are shown in Figs. 3(a) and 3(b) for the Al-H (-D) complexes at several temperatures. The vibrational band also narrows and shifts to higher frequency upon cooling from room temperature to ∼5 K. At room temperature there is a broad band centered at 2100 cm^{-1} with a FWHM of 110 cm^{-1}. At liquid-He temperature the band shifts to 2201 cm^{-1} and has a FWHM of 9.2 cm^{-1}. However, for Al-H a sideband is clearly observed at 2162 cm^{-1}, 39 cm^{-1} to the low-energy side of the main vibrational band for intermediate temperatures. A similar sideband occurs for the Al-D complex at 1570 cm^{-1}, 27 cm^{-1} from the main band at 1597 cm^{-1}. These sidebands indicate that there is a low-energy excitation of the Al-H (-D) complex that gives rise to structure in the ground vibrational state that can be thermally populated. The effect of the isotopic substitution, D for H, upon the frequency difference between the main band and sideband establishes that the low-frequency excitation involves the motion of H in the complex.

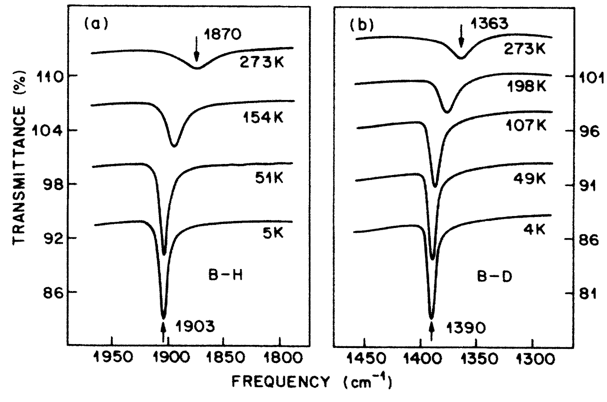

FIG. 2. Hydrogen stretching vibration as a function of temperature for (a) B-H and (b) B-D complexes in silicon.

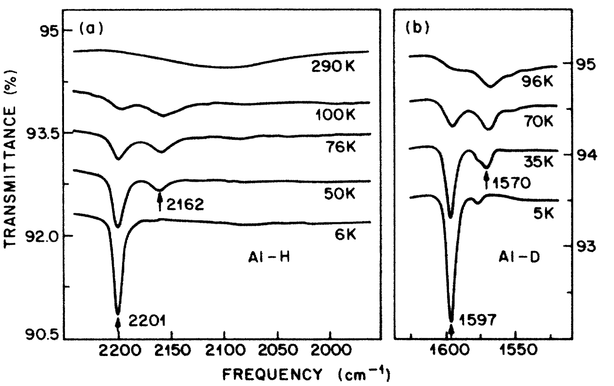

FIG. 3. Hydrogen stretching vibration as a function of temperature for (a) Al-H and (b) Al-D complexes in silicon. The small feature for Al-D at 5 K near 1575 cm^{-1} has no counterpart in the Al-H spectrum and is presumed to be unrelated to the Al-D complex.

Spectra are shown in Figs. 4(a) and 4(b) for Ga-H and Ga-D complexes. The vibrational bands are at 2171 and 1577 cm^{-1} for Ga-H and Ga-D, respectively. There are also low-energy sidebands for the Ga-H (-D) complexes. For the Ga-H complex the sideband structure is only partially resolved. At the lowest temperatures the vibrational bands are broad and asymmetric as was the case for the B-H (-D) complexes.

We note that there was a broad ($\sim$50-cm^{-1}) temperature-independent feature centered at 2100 cm^{-1} in the Ga sample. To cancel this feature in the spectra shown we used the room-temperature Ga-H spectrum as the reference. There was no corresponding broad feature in the Ga-D spectrum.

IV. LOW-FREQUENCY EXCITATIONS

The thermally populated sidebands which appear in our spectra for Al-H (-D) and Ga-H (-D) complexes are reminiscent of the rich vibrational spectrum of interstitial oxygen in silicon.[20,21] Interstitial oxygen bridges two silicon atoms in the lattice and is bent slightly off the ⟨111⟩ axis. The antisymmetric stretching mode of this Si-O-Si "defect molecule" gives rise to a very sharp band at 1136 cm^{-1} at liquid-He temperature. As the temperature is elevated, a series of thermally populated sidebands appear on the low-energy side of the main vibrational band until at room temperature there is a broad (FWHM of 30 cm^{-1}), featureless band at 1106 cm^{-1}. Bosomworth *et al.*[21] showed that the slightly-off-axis interstitial oxygen has a low-frequency (29-cm^{-1}) bending vibration that gives rise to the fine structure in the higher-frequency antisymmetric mode absorption. We adopt a similar model to explain the sidebands we observe in our acceptor-H spectra. We propose that the sidebands are due to a low-energy motion of the acceptor-H complex that gives rise to fine structure on the H stretching vibration. The thermal population of this ladder of states associated with the vibrational ground state causes the pronounced shift and broadening of the H stretching band as the temperature is elevated.

For more detailed study we focus on Al-H (-D) because the sidebands are clearly resolved for these complexes. The energy splitting between the main vibrational band and the sideband is not necessarily the excitation energy of the low-frequency motion. Hence, we determine the Boltzmann energy by examining the thermal population of the sideband. The main band and its sideband can be fitted well by Lorentzian curves. Typical fits are shown in Fig. 5. From the parameters of such fits we determine the ratio of sideband to main-band area, I_1/I_0, which is proportional to the Boltzmann factor

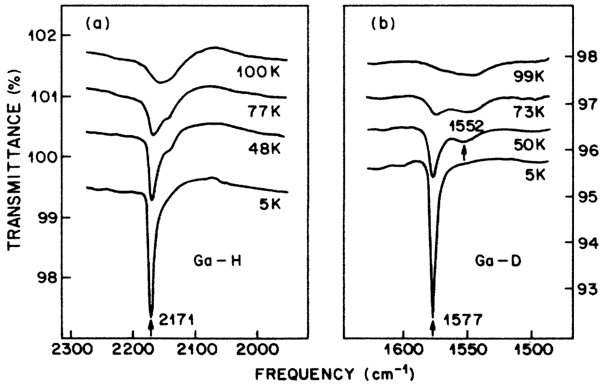

FIG. 4. Hydrogen stretching vibration as a function of temperature for (a) Ga-H and (b) Ga-D complexes in silicon.

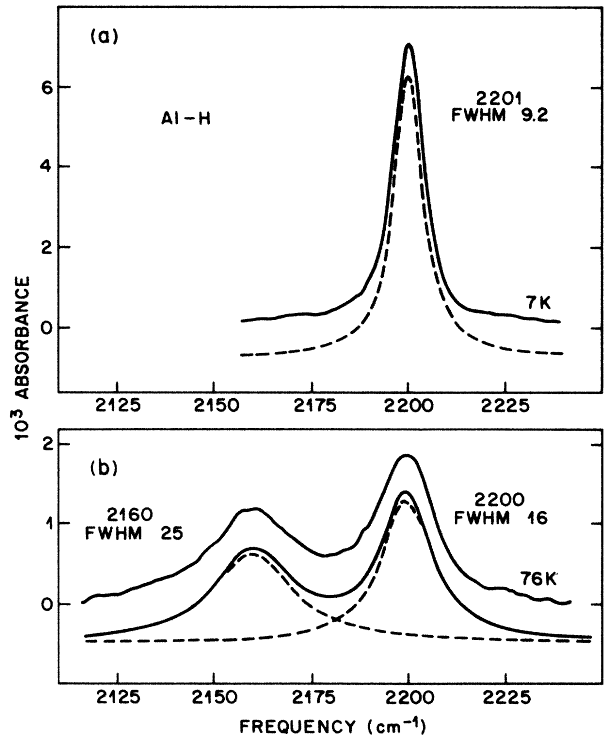

FIG. 5. Typical Lorentzian fits to the Al-H line shape at two temperatures. The measured line shape is shown above and the fits are shown below. The band frequency and FWHM for the fit are also shown.

$$I_1/I_0 \propto e^{-E_A/k_BT} \, .$$

We plot $\ln(I_1/I_0)$ versus T^{-1} to determine E_A in Fig. 6. For Al-H the slope of the plot gives $E_A(\mathrm{H})=78\ \mathrm{cm}^{-1}$.

The difference between the Boltzmann energy we have measured, 78 cm^{-1}, and the energy splitting between the main vibrational band and sideband, 39 cm^{-1}, leads us to the simple model shown in Fig. 7 for the transitions. The energy spacing of the fine structure in the excited vibrational state is less than that in the ground vibrational state, leading to the energy splitting in the spectral transitions. The situation for interstitial oxygen in Si is similar, but much more is known about the low-energy excitation for oxygen from the detailed far-infrared data.[21] We expect that the vibrational potential surfaces are more complicated than we have drawn for Al-H, but we have insufficient data to go further.

We have determined the Boltzmann energy for the low-frequency excitation of the Al-D complex by a similar procedure as for Al-H. A plot of $\ln(I_1/I_0)$ versus T^{-1} is shown in Fig. 6 for Al-D. The Boltzmann energy $E_A(\mathrm{D})$ is 56 cm^{-1}. The ratio $r=1.39$ [where $r \equiv E_A(\mathrm{H})/E_A(\mathrm{D})$] is close to $(M_\mathrm{D}/M_\mathrm{H})^{1/2}$, as is expected if the low-energy motion is an ordinary vibration.

Strong evidence for low-energy (~1-meV) tunneling motions was presented for the Be-H (-D) centers in silicon. For this case a giant isotope effect (characteristic of a tunneling splitting), $r=2.5$, was observed by far-infrared absorption.[19] For Al-H (-D) there is no giant isotope effect observed and hence there is no evidence for tunneling for these complexes, contrary to our earlier speculation.[12] While our data do not provide evidence for tunneling, it is possible that similar degrees of freedom are involved for the tunneling motions of Be-H complexes and the group-III-acceptor–H complexes studied here. A change in the parameters that characterize the atomic potential surfaces could change the motion from one with pronounced tunneling characteristics to an ordinary vibration.

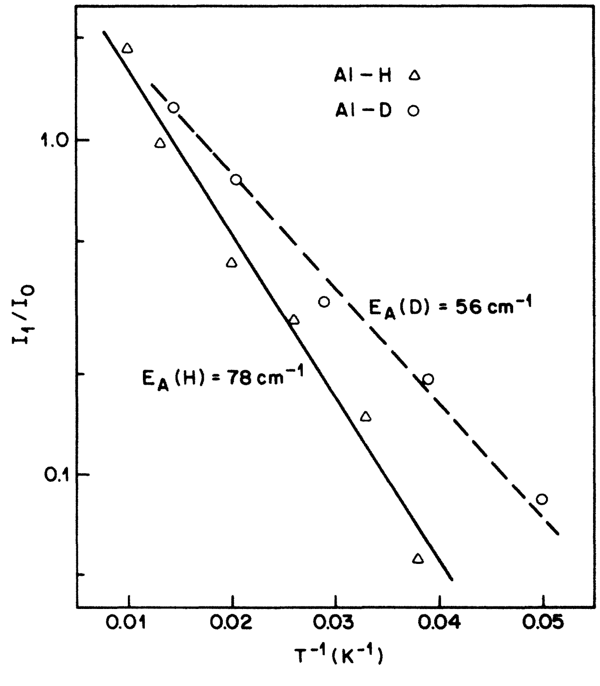

FIG. 6. The ratio of sideband to main-band area, I_1/I_0, vs (temperature)$^{-1}$.

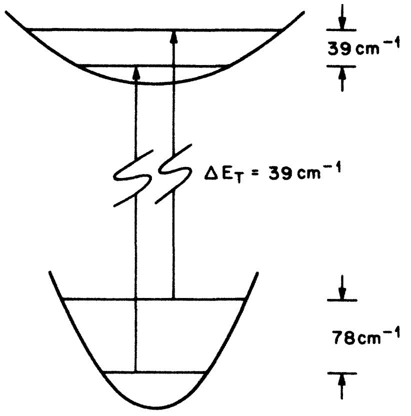

FIG. 7. A model for the sharp vibrational band observed for Al-H complexes at liquid-He temperature and the sideband observed at intermediate temperature. The lower parabola is for the ground state of the H stretching vibration and the upper parabola is for the excited vibrational state. The low-energy motion of the complex adds fine structure to these states.

For Ga-H a shoulder appears on the main vibrational band upon warming up from liquid-He temperature and for Ga-D a sideband appears at 25 cm^{-1} to lower energy from the main band. Thus, although we have not examined the Ga-H (-D) complexes in as much detail as for Al-H (-D), they clearly behave similarly. For B-H (-D) no additional structure is seen upon warming from liquid-He temperature; however, the bands at 1903 and 1390 cm^{-1} for B-H and B-D, respectively, shift and broaden dramatically upon warming. Hence we suspect that the same low-frequency motions are responsible for the shift and broadening, but sidebands are not resolved for the fairly broad B-H (-D) bands.

V. LINE SHAPE OF THE ACCEPTOR-H BANDS

We have noted that the acceptor-H bands are broad and asymmetric. We make a few qualitative remarks about the line shapes here.

Several effects might give rise to broad lines in heavily implanted layers. Residual implant damage is perhaps the most obvious. Another possibility is that the large concentration of implanted species shifts vibrational frequencies because the different size of the implanted ions affects the average lattice constant of the host crystal. The concentration of implanted acceptors varies with depth; hence the vibrational frequencies should also vary with depth and give rise to line broadening. Rough estimates show that such concentration effects can give rise to frequency shifts and linewidths of a few cm^{-1} for peak acceptor concentrations of $\sim 10^{20}\ \mathrm{cm}^{-3}$. Finally, we suggest that the acceptor-H vibrational bands are broadened by a Fano interaction[22] with the continuum absorption

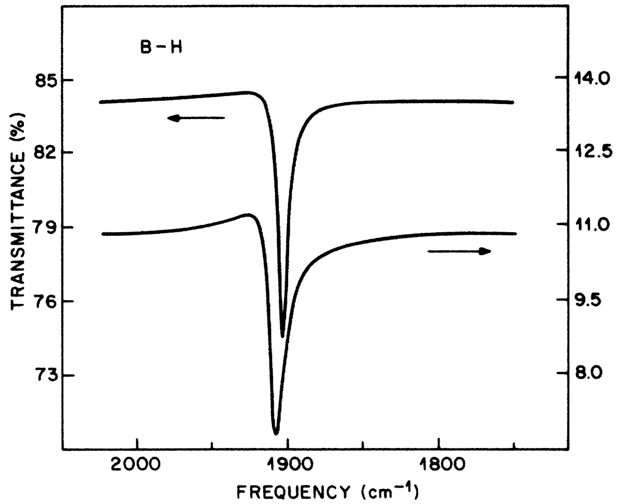

FIG. 8. Line shapes of the Si-H stretching vibration for the B-H complex for different acceptor implant doses. The peak B concentration was 3×10^{19} cm^{-3} for the upper spectrum and 2×10^{20} cm^{-3} for the lower.

due to residual free carriers and that these effects dominate the line shapes for our samples.

Fano-interaction effects are well known in Raman studies of heavily doped materials.[23–25] Both the Si optical phonon[23] at 520 cm^{-1} and the B local-mode features[24] at 620 and 644 cm^{-1} show pronounced Fano-interaction effects with free-carrier scattering at acceptor concentrations of $\sim10^{19}$ cm^{-3} and greater. At an acceptor concentration of 10^{20} cm^{-3} broad asymmetric lines with widths of $\gtrsim 20$ cm^{-1} are typical.

The change in line shape with doping provides strong evidence that the interactions of the acceptor-H vibration with the residual free-carrier continuum dominates the line shapes we have observed. The Al-H line shape [Fig. 5(a)] is the most symmetric of the different acceptor-H bands. The Al concentration was also the lowest and the passivation of the Al acceptors the most complete. The asymmetry and line broadening are more pronounced for an increased acceptor concentration, as we show for boron in Fig. 8. The samples for the upper and lower spectra had peak free-carrier concentrations before plasma exposure of 3×10^{19} and 2×10^{20} cm^{-3}, respectively, as measured by spreading resistance. Also note the difference in residual free-carrier absorption. While 75% of the acceptors in the lower-concentration sample are passivated, only ~40% are passivated in the higher-concentration sample, as determined by spreading resistance. The upper spectrum has a width of 9 cm^{-1}, while the lower spectrum has a width of ~14 cm^{-1}. For the higher acceptor concentration the line shape has classic Fano-resonance characteristics.

Infrared studies of complexes that result from shallow-level passivation are most conveniently performed on heavily doped surface layers because of the limited diffusion depth of H at temperatures where such complexes are stable. We expect that Fano interactions will contribute generally to linewidths and band asymmetry, and will shift peak positions in such experiments.

VI. CONCLUSION

In summary, an unexpected low-frequency excitation of acceptor-H complexes has been observed through the sideband structure it gives rise to in the infrared-absorption spectra of the ~2000-cm^{-1} H stretching vibrations. The temperature dependence of the sideband intensity leads to energies of 78 and 56 cm^{-1} for the low-frequency excitations of the Al-H and Al-D complexes, respectively. This isotope effect establishes that the low-frequency excitation involves H motion and is consistent with an ordinary low-frequency vibration rather than a tunneling splitting.

We suggest two possibilities for what the low-frequency motion of the acceptor-H complex might be, both in the context of the configuration of Pankove *et al.*[4] By analogy with interstitial oxygen, where the slight buckling of the Si-O-Si unit gives rise to low-frequency motions of the O about the ⟨111⟩ axis, we suggest that the H may be off axis for the acceptor-H–Si unit. With the H off axis, the low-frequency excitation would be due to the characteristic motion of a nearly linear molecule.[26] As a second possibility we suggest that the H may be moving between the different ⟨111⟩ directions about the acceptor atom. If the acceptor is slightly displaced by the H, as found in the calculation of DeLeo and Fowler,[5,6] it would also move as the H moves between ⟨111⟩ directions. Hence this would be essentially a hindered rotation of the acceptor-H unit.

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