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Donor-hydrogen complexes in passivated silicon

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Several new infrared absorption bands have been discovered in hydrogen passivated silicon doped with P, As, and Sb. The frequency shift upon substitution of D for H confirms the assignment of these bands to donor-H complexes. Thermal annealing experiments, in which both the absorption due to complexes and to free carriers were measured, confirm that donor passivation is due to complex formation, and yield the stability of the complexes. Our results suggest that H is bonded to Si rather than the donor directly.

There is much interest in the passivation of shallow impurities in semiconductors by hydrogen.[1] In silicon, acceptor neutralization is well known.[2,3] Recently, partial donor passivation in silicon has been reported by Johnson and co-workers[4] for P surface layers that were H_2 plasma exposed and examined by Hall-effect measurements. From the increase in the Hall mobility it was inferred that complex formation rather than compensation was responsible for the donor neutralization by hydrogen. While models for donor-H complexes were proposed and vibrational frequencies predicted,[4] there are no data that provide microscopic information.

Vibrational spectroscopy has provided an excellent probe of shallow level-H complexes in Si and GaAs and has helped establish microscopic models for the passivation process.[5-8] Here, we report the observation of vibrational absorption due to donor-H (or D) complexes in Si for P, As, and Sb donors. Annealing experiments confirm that passivation is due to complex formation and also give the stability of the donor-H complex.

Our samples were prepared by the implantation of P, As, or Sb into float-zone silicon wafers with ion energies of 30, 100, and 200 keV, a typical dose of 10^{15} cm^{-2} for each energy, and an activation anneal of 1150 °C for 30 s. The implanted layers were typically 0.2 μm thick. The implanted wafers were exposed to an H_2 (or D_2) plasma for up to 6 h at 120 °C. Infrared absorption spectra were measured with a Nicolet 60SX Fourier-transform spectrometer at a resolution of 1 or 2.5 cm^{-1}. For low-temperature measurements an Air Products Helitran cryostat was used. During the annealing experiments reported below we observed an anomalous growth of Sb-H complexes before their dissolution. Mild etching removed this anomaly without affecting other sample properties.

Donor passivation was confirmed by spreading resistance measurements. Sheet carrier concentration reductions of 52%, 83%, and 82% for P, As, and Sb were observed. The weaker passivation of P is explained by the instability of the P-H complex reported below at the hydrogenation temperature, 120 °C. The free-carrier absorption was also reduced in the hydrogenated samples.

Hydrogenated or deuterated samples for each donor show three absorption bands. Their frequencies, widths, and relative strengths are given in Table I. Figure 1(a)

TABLE I. Frequencies, linewidths, and relative intensities for the absorption bands of P, As, and Sb donor-H (-D) complexes in silicon. The linewidths were measured at 1 cm^{-1} resolution, thus all bands were not completely resolved; the relative intensities were normalized to the intermediate energy band for each combination of donor and hydrogen isotope separately. Also included are the frequency ratios of corresponding bands for H and D. These data were measured at liquid-He temperature.

	H_2 plasma			D_2 plasma			
	Frequency (cm^{-1})	FWHM (cm^{-1})	Relative strength	Frequency (cm^{-1})	FWHM (cm^{-1})	Relative strength	Frequency ratio
Si:P	809.4	1.7	1.9	584.7	1.6	2.6	1.384
	1555.2	3.7	1	1141.4	1.8	1	1.363
	1647	10	0.2	1216	4.6	2.2	1.354
Si:As	809.8	1.4	1.7	584.8	1.4	2.3	1.385
	1561.0	2.7	1	1143.0	2.2	1	1.366
	1661	9	0.2	1222	4.5	3.3	1.359
Si:Sb	809.6	1.4	1.6	584.0	1.7	2.3	1.386
	1561.7	2.1	1	1142.8	1.7	1	1.367
	1671	9	0.6	1218	4.3	2.7	1.372

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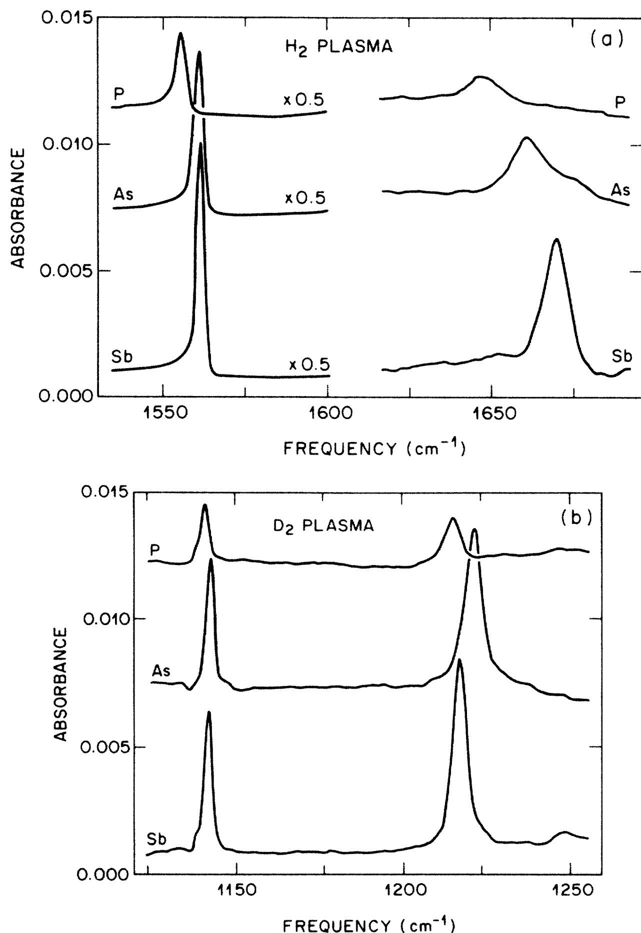

FIG. 1. Absorption bands in P-, As-, and Sb-doped silicon samples that have been passivated in (a) an H_2 plasma and (b) a D_2 plasma. The sharp bands to the left are assigned to H (D) bond-stretching vibrational modes of donor-H (-D) complexes. The broader bands to the right increase dramatically in relative strength upon isotopic substitution (D for H), and are assigned to another donor-H (-D) complex, possibly incorporating a plasma-related defect. The spectra were recorded at liquid-He temperature.

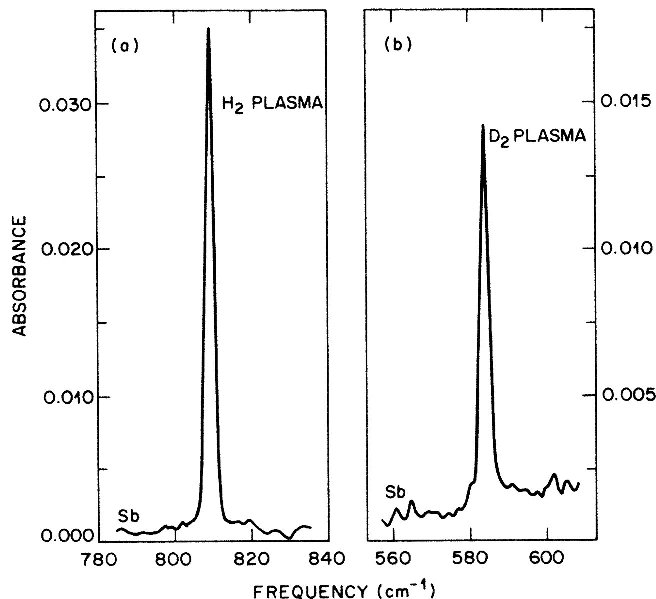

FIG. 2. Absorption bands in Sb-doped silicon that has been passivated in (a) an H_2 plasma and (b) a D_2 plasma. Samples containing P or As donors show virtually identical bands, which are assigned as bond-bending vibrational modes of donor-H (-D) complexes. The spectra were recorded at liquid-He temperature.

shows two near-lying bands for the three hydrogenated donor implants, and Fig. 1(b) the corresponding bands for deuterated samples. The third band at 809 cm^{-1} has nearly identical frequency and width for the different donors. Figures 2(a) and 2(b) show this band for Sb-H and the corresponding band for Sb-D complexes as an example.

The vibrational bands shown in Figs. 1 and 2 only appear in donor-implanted samples. When D is substituted for H all bands show shifts that demonstrate that the vibrations involve hydrogen motion. Thus, we assign all bands to complexes that contain at least the donor and hydrogen. Further, no additional bands were observed in samples subjected to a plasma containing both H_2 and D_2; thus only one hydrogen atom is incorporated in the complexes.

The lines near 809 and 1560 cm^{-1} for the H-containing complexes have an approximate 2:1 ratio of intensities in all samples. Similar results are obtained for the donor-D spectra. Hence we assign these two lines to doubly degenerate bond-wagging and nondegenerate bond-stretching vibrational modes of donor-H (or -D) complexes. The donor and H atoms are presumably the only defects involved in these complexes.

The intensity of the broad feature near 1660 cm^{-1} varies relative to the bands near 809 and $\sim$1560 cm^{-1} for the different donors. The corresponding feature at 1220 cm^{-1} for the D_2 plasma exposure is much stronger than for the H_2 plasma for each donor, leading us to suggest that the $\sim$1660-cm^{-1} band is related to another complex. We discuss the 1660-cm^{-1} band at the end of the text and refer only to the 809- and $\sim$1560-cm^{-1} bands in what follows, unless stated otherwise.

The line positions shift less than 1 cm^{-1} for sample temperatures from 4.2 to 100 K. The stretching bands show approximately a factor of 2 increase in width at 100 K, while the wagging bands remain nearly as sharp as at 4.2 K. The wagging bands were easily detected at room temperature.

We note the asymmetry in the line shape of the stretching bands in Fig. 1(a), which has been reported previously for other defect-H complexes.[6,9] The isotopes ^{29}Si and ^{30}Si will give weak, unresolved shoulders to the low-energy side of the vibrational band and hence will contribute to the asymmetry. As was suggested previously for acceptor-H complexes,[9] another cause of the asymmetric line shape might be Fano resonance,[10] i.e., the mixing of a discrete state and a continuum. The continuum in this case is due to residual free carriers. The asymmetry is less

pronounced in samples with lower donor concentrations.

The strength of a vibrational transition is often expressed as an effective oscillating charge q, defined by the expression[11,12]

$$\int \alpha(E)dE = \frac{2\pi^2\hbar q^2 N}{cnM} . \tag{1}$$

Here we determined the concentration of centers N from our spreading resistance profiles and take the vibrating mass M to be the proton mass. The integrated absorption coefficient $\int \alpha(E)dE$ includes the areas of the bands near 809 and 1560 cm^{-1}, and n is the refractive index. For P-H complexes we obtain $q = 0.9e$; for As-H, $q = 1.2e$; and for Sb-H, $q = 0.9e$; e being the electron charge. These values compare well with those for Si-H complexes in GaAs (Ref. 6) and other local-mode absorptions in Si.[12] Hence, the number of complexes we observe optically is consistent with the carrier removal we measure electrically.

We have performed annealing experiments in which the areas of the vibrational bands were measured to determine the change in concentration of donor-H complexes. The free-carrier absorption was measured to monitor the return of donor electrical activity. If we assume that the donor-H complexes dissociate irreversibly during annealing, then the number of complexes present, N_H, is given as a function of the annealing time t and temperature T by the expression[13]

$$N_H/N_0 = \exp(-kt) , \tag{2a}$$

where

$$k = \nu\exp(-E_d/kT) . \tag{2b}$$

Here N_0 is the initial concentration of centers, ν is the attempt frequency, and E_d the binding energy. We performed an isothermal annealing experiment at 423 K for the As-H complex and confirmed the exponential decay expressed in Eq. (2a) for a 50 times reduction in concentration. In Fig. 3 are shown the results of a series of 30-min isochronal anneals. The curves are given by Eq. (2), with an assumed attempt frequency of 10^{13} s^{-1} and binding energies of 1.32 eV for P-H and 1.43 eV for As-H and Sb-H.

During the annealing experiments there was a concomitant increase in the free-carrier absorption as the concentration of donor-H complexes decreases. After the donor-H complexes had fully dissolved, further annealing (we checked up to 400 °C) did not increase the free-carrier absorption additionally. These results further confirm that the complexes whose spectra are reported here are responsible for the donor passivation.

Comparing the frequencies of the wagging and stretching bands for the three donor-H complexes shows that only the stretching mode of the P-H center differs appreciably from the other centers. (For B-H and Al-H complexes in Si,[8,9] the stretching frequencies differ by nearly 300 cm^{-1}.) The small shift of the vibrational frequencies among the different donor-H complexes suggests that the H is not attached directly to the donor atom. The stretching frequencies of the donor-H complexes are lower than

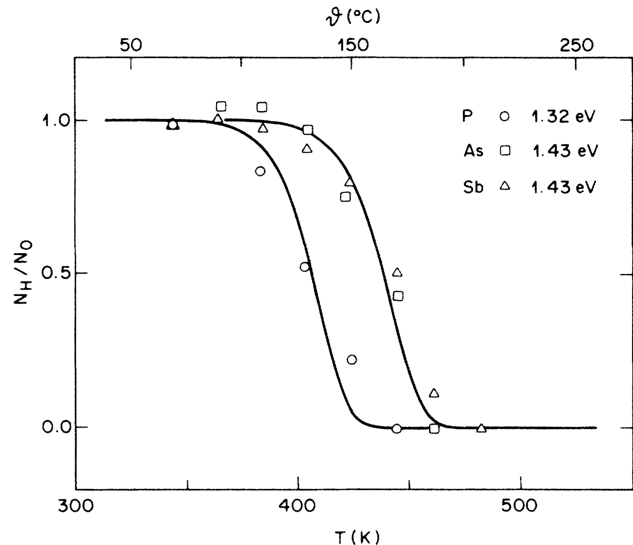

FIG. 3. The normalized concentration of donor-H complexes that remains after 30-min anneals at successively higher temperatures. The solid lines are drawn according to Eq. (2) in the text, using an attempt frequency of 10^{13} s^{-1} and the binding energies shown. Data shown are for the stretching band near 1560 cm^{-1}.

for acceptor-H complexes in Si. Shallow level-H complexes in GaAs (Refs. 6 and 14) have similar characteristics, suggesting similarities in the passivation mechanisms in the two materials.

The ratio $r = \omega(H)/\omega(D)$ of the frequencies obtained for donor-H and -D complexes are presented in Table I. The ratio $r = 1.390$ is calculated from the reduced masses of Si-H and -D. The wagging modes have r's near this value. The smaller values observed for the stretching bands compare favorably to values previously quoted for Si—H bonds.[6] The r's for the wagging and stretching vibrations of the different complexes are nearly equal and support models with H bound to Si because r does not change with the donor mass.

Johnson, Herring, and Chadi,[4] have proposed a model for the donor-H complex where the hydrogen atom is attached to one of the donor's nearest neighbors and occupies the antibonding position along the ⟨111⟩ axis containing the donor atom. For this model the vibrations of the hydrogen atom might be insensitive to the identity of the donor because it is not bonded to it, consistent with our results. Such a configuration would have trigonal symmetry and is consistent with the doubly degenerate wagging vibration observed.[15] However, our vibrational frequencies are in marked disagreement with the calculations of Johnson *et al.*[4] for this model, which predict a stretching frequency near 2100 cm^{-1}. No absorption band due to hydrogen was detected in our samples near that frequency.

Finally, we return to the broad bands near 1660 cm^{-1} in Fig. 1(a), which we attribute to a different complex. As may be seen from Table I, the frequencies of these bands are sensitive to the chemical identity of the donor. Further, the isotropic substitution ratio r increases with

the donor mass. These results suggest that the H is bonded to the donor. The relative strength of the 1220-cm^{-1} band obtained for D_2 plasma exposure is much greater than that of the 1660-cm^{-1} band. The heavier isotope should create more defects during the plasma treatment, suggesting a complex that involves the donor, H (or D), and an additional plasma-related defect, e.g., a vacancy. Further experiments will be necessary to identify the complex. We note that the 1660-, 1560-, and 809-cm^{-1} bands show similar annealing characteristics.

In conclusion, we have reported vibrational spectra for donor-H complexes for P, As, and Sb donors in passivated *n*-type silicon, and have shown directly that the passivation takes place through complex formation. The passivation of 80% of the donors in thin (0.2 μm) layers is attainable for appropriate plasma exposure conditions. Our data lead us to assign two lines at 809 (584) and $\sim$1560 ($\sim$1142) cm^{-1} to the wagging and stretching modes of donor-H (-D) complexes with the H (D) atom bonded to Si. An additional line at $\sim$1660 ($\sim$1220) cm^{-1} is tentatively assigned to another complex that includes a plasma-related defect. Annealing experiments show that the donor-H complexes have binding energies of 1.32 eV for P-H and 1.43 eV for As-H and Sb-H.

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