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High-resolution infrared study of the neutralization of silicon donors in gallium arsenide

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High-resolution infrared spectroscopy has been used to study the effects of hydrogen and deuterium plasma passivation of silicon donors in epitaxial layers of GaAs grown by metalorganic chemical-vapor deposition (MOCVD). In addition to the lines at 896 cm^{-1} (1-H) and 647 cm^{-1} (1-D) reported by Jalil *et al.* two new infrared absorption lines at 1717 cm^{-1} (2-H) and 1248 cm^{-1} (2-D) which show isotope shifts from paired ^{28}Si, ^{29}Si, and ^{30}Si are found in samples passivated by hydrogen and deuterium, respectively. It is proposed that a bond between an interstitial H atom and a Si_{Ga}^{+} impurity is formed which includes the donor electron, creating a pair defect with C_{3v} point-group symmetry. Line 1-H is ascribed to a doubly degenerate transverse mode and line 2-H to a nondegenerate longitudinal stretching mode of the paired hydrogen. Neutralization of the Si_{Ga} donors is indicated by a reduction of the carrier concentration from 4×10^{18} cm^{-3} to about 10^{17} cm^{-3}, and a corresponding reduction is observed in the strength of the localized vibrational mode (LVM) line due to isolated Si_{Ga} at 384 cm^{-1}. Two new vibrational modes of the paired silicon are predicted with a small isotope shift when H is replaced by D. So far, one mode has been observed from Si_{Ga}-H at 409.95 cm^{-1} and Si_{Ga}-D at 409.45 cm^{-1}.

I. INTRODUCTION

Hydrogen can be diffused a few micrometers into most semiconductors by exposing them to a H plasma. In GaAs, this treatment has been shown to neutralize (or passivate) partially or totally the donors present in n-type material[1] and also Zn acceptors[2] in p-type layers These effects, which are assumed to take place via chemical binding of hydrogen can be annealed out near 400 °C. The temperature dependence of the recovery of the electrical activity can give information on the strength of the binding for different chemical donors.[3] Passivation is also produced with a deuterium plasma but not with helium.[1,4] It has already been shown[5] that a vibrational absorption band at 890 cm^{-1} (300 K), now designated 1-H, is produced in H-passivated Si-doped GaAs. The attribution of this band to hydrogen is confirmed by the observation of a band at 640 cm^{-1} (1-D) in deuterium-passivated material as the ratio r_1 of 1.39 for the two frequencies is close to the square root of the ratio of the atomic masses.

The purpose of this paper is to present the results of further infrared investigations of Si-doped GaAs neutralized by hydrogen in an attempt to obtain a better understanding of the passivation process.

II. EXPERIMENTAL RESULTS

n-type GaAs:Si epilayers with Si concentrations between 3×10^{18} and 4×10^{18} at. cm^{-3} were deposited by MOCVD (metalorganic chemical-vapor deposition) on (100) GaAs semi-insulating (si) substrates. The electrical activity of the layers was substantially reduced by exposure to either a hydrogen or deuterium plasma.[5] The electron mobility at 300 K of the epilayer with $n\simeq3\times10^{18}$ cm^{-3} before passivation was 1800 $cm^2\,V^{-1}\,s^{-1}$, indicating a compensation ratio[6] $\simeq0.4$. It is inferred that compensating acceptors and/or deep centers were present which may include intrinsic defects such as vacancy complexes and antisite defects. After the passivation process, the 300-K mobility of 2490 $cm^2\,V^{-1}\,s^{-1}$ was consistent with a residual donor concentration of $\simeq1\times10^{17}$ cm^{-3} with a compensation ratio of 0.7. Hence the effect of hydrogenation is a strong reduction of the concentration of both the donors and the compensating centers.[7] Transmission spectra of the passivated samples held near liquid-helium temperature (LHeT) were obtained down to 430 cm^{-1} using a BOMEM DA3-01 Fourier-transform spectrometer (FTS) with an extended-range mercury cadmium telluride (MCT) detector. To avoid mounting stresses, the specimens were

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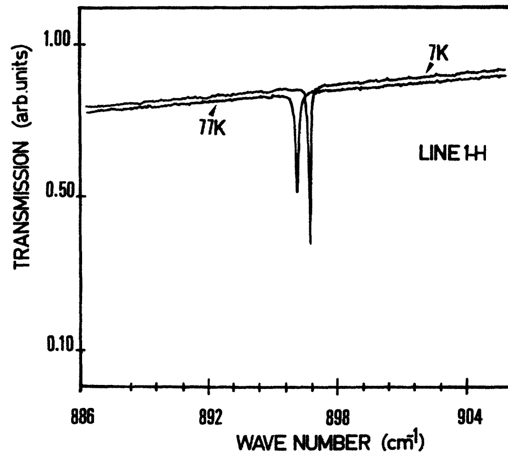

FIG. 1. Transmission of a 4-μm-thick H-passivated GaAs:Si single epilayer on a si substrate in the vicinity of the 1-H. Before passivation, $n \simeq 3 \times 10^{18}$ cm^{-3}. The apodized resolution is 0.05 cm^{-1} and one abscissa division is 1.2 cm^{-1}.

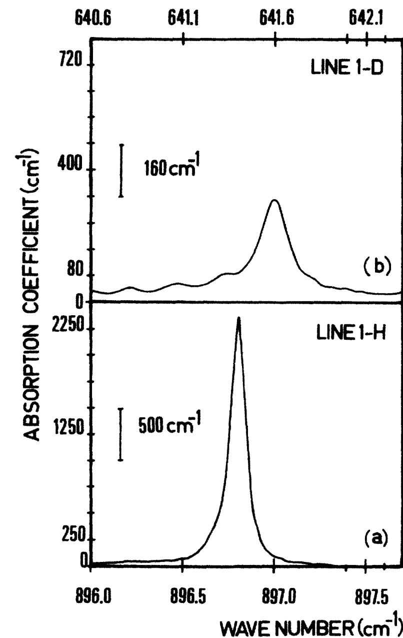

FIG. 2. (a) Absorption coefficient of line 1-H at 6 K in passivated GaAs:Si with an apodized resolution of 0.05 cm^{-1}. Note the low-energy side asymmetry of the line. Before passivation, $n \simeq 5 \times 10^{18}$ cm^{-3}. (b) Same as (a) for line 1-D.

free-standing in the sample compartment of an Oxford Instrument Model CF 204 cryostat. Their temperature was measured with a germanium thermometer placed in the sample compartment at the same level as the sample. Transmission spectra in the range 200–650 cm^{-1} were obtained near LHeT and with a resolution of 0.1 cm^{-1} using a Bruker 113v FTS equipped with a bolometer detector.

The present high-resolution measurements show that lines 1-H at 896.8 cm^{-1} and 1-D at 641.6 cm^{-1} are very narrow, so they also appear to be very intense. Figure 1 shows the 1-H line with the sample at 7 and 77 K, respectively, and reveals a temperature-dependent frequency shift of 0.570 cm^{-1}. This shift is more than twice as large as the shift of the C_{As} localized vibrational modes (LVM's) near 582 cm^{-1} (0.263 cm^{-1}). For an unapodized (boxcar) resolution of 0.024 cm^{-1}, the measured full width at half-power (FWHP) of 1-H at 6 K is 0.085 cm^{-1} for the sample with [Si]$\simeq 4 \times 10^{18}$ at. cm^{-3}. However, the FWHP extrapolated from the high-energy side of 1-H is $\simeq$0.07 cm^{-1}, indicating a broadening of the low-energy side as shown in Fig. 2(a). This asymmetry will be discussed again later. Line 1-D is about twice as broad as line 1-H for the same conditions of observation, but there is again a broadening on its low-energy side [Fig. 2(b)]. From the positions of lines 1-H and 1-D a

TABLE I. Position (cm^{-1}) of the hydrogen and deuterium related lines in passivated GaAs:Si at different temperatures. r is the ratio of the frequency of the hydrogen and deuterium lines. ND denotes not detected.

Line	6 K	77 K	294 K
1-H	896.815±0.003	896.245±0.004	889.89±0.05
1-D	641.519±0.006		636.75±0.03
r_1	1.397 96±0.000 02		1.3976±0.0002
2-H (^{28}Si)	1717.252±0.004	ND	ND
2-H (^{29}Si)	1716.890±0.008		
2-H (^{30}Si)	1716.531±0.009		
2-D (^{28}Si)	1247.613±0.008		
2-D (^{29}Si)	1247.08±0.15		
r_2 (^{28}Si)	1.376 43±0.0000 82		
r_2 (^{29}Si)	1.3767 ±0.0002		
^{28}Si$_{\mathrm{Ga}}$—H	409.95		
^{28}Si—D	409.45		

highly accurate value of $r_1 = \nu_{1\text{-H}}/\nu_{1\text{-D}}$ is obtained (Table I). During a run the average temperature variation was ±0.3 K. For line 1-H, the corresponding frequency uncertainty is ±0.008 cm^{-1} when extrapolated linearly from the line shift between 6 and 77 K. This shift however is not linear with temperature in the whole range and the above extrapolation overestimates the uncertainty near LHeT: The total frequency excursion on line 1-H near 6 K observed for ten measurements on two different samples was 0.002 cm^{-1} and this was taken into account when estimating the uncertainty given in Table I for this line.

A second line (2-H) at 1717.25 cm^{-1} has now been observed in hydrogen-passivated GaAs:Si. It is located near a residual water vapor line at 1717.406 cm^{-1} and the two lines can be separated only under high-resolution conditions. Its assignment is confirmed by the observation of a corresponding line (2-D) at 1247.64 cm^{-1} (6 K) in a sample exposed to a deuterium plasma (Fig. 3). Line 2-H has a value of FWHP of 0.16 cm^{-1} while the value for line 2-D is 0.37 cm^{-1} so that the ratio of the widths is similar to that for lines 1-H and 1-D. The lines 2-H and 2-D are weaker than lines 1-D and 1-H, with a ratio of integrated absorptions $A_I(\text{1-H})/A_I(\text{2-H})$ approximately equal to three. The widths of lines 2-H and 2-D increase rapidly with increasing temperature. At 29 K, the maximum absorption of line 2-H is smaller by a factor of about 3 compared with its value at 6 K and there is a corresponding increase in the width. The temperature-dependent shift of line 2-H near LHeT is 0.009 cm^{-1}/K. At 77 K, the line can hardly be detected. It should be noted that this strong temperature dependence of the intensity of line 2-H is in marked contrast to that found for (a) a line at 2147 cm^{-1} (6 K) associated with a hydrogen atom near a zinc acceptor[8] in GaAs where the line can still be observed[9] up to 200 K, and (b) for lines attributed to hydrogen complexed with transition metals and/or native defects and observed[10] in III-V compounds between 2000 and 2300 cm^{-1} as the FWHP of these lines is still less than 0.5 cm^{-1} at 200 K. The frequency ratio r_2 (Table I) is comparable with that found for H- and D-related lines observed in *c*-Si grown in hydrogen or deuterium atmospheres,[11] in H^+- and D^+-implanted *c*-si, and in H- and D-passivated *p*-type *c*-Si (Refs. 12 and 13). (Table II shows that the difference between the LHeT positions of the B-related lines in silicon near 1905 cm^{-1} reported by two different groups is instrumental, as the frequency shift of this line near LHeT is less than 0.025 cm^{-1}/K.) This similarity suggests that line 2 could arise from the vibrations of H or D atoms bound directly to silicon atoms. Silicon has three naturally occurring isotopes, ^{28}Si, ^{29}Si, and ^{30}Si with relative abundances of 92.2%, 4.7%, and 3.1%. Hence if line 2 is due to a Si-H or Si-D vibration, three components are expected with intensities scaling with the isotopic abundances. Such an isotope effect was observed in samples with an increased Si concentration and an epilayer deposited on each side of the

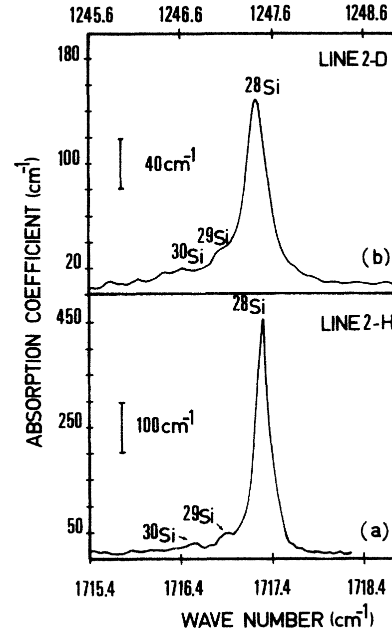

FIG. 3. Absorption coefficient of lines (a) 2-H and (b) 2-D at 6 K in the same samples as for Fig. 2. The apodized resolution is 0.10 cm^{-1}.

TABLE II. Frequency (cm^{-1}) of the pure and "mixed" Si-related stretching mode in hydrogenated and deuterated crystalline silicon.

	T (K)	H-related	D-related	r
Undoped[a]	10	2223	1617	1.3748
	Ambient	2210	1604	1.378
Undoped	10	1952	1421	1.3737
	Ambient	1946	1417	1.373
B-doped[b]	LHeT	1907	1392	1.370
B-doped[c]	7	1904.81	1390.69	1.3697
B-doped[d]	Ambient	1870	1360	1.375
Al-doped[b]	LHeT	2201	1596	1.379
Ga-doped[b]	LHeT	2171	1577	1.378

[a]Reference 11. The two values refer to two different centers.
[b]Reference 12.
[c]Pajot, unpublished results.
[d]Reference 13.

substrate (Fig. 3). The Si isotope effect for the ^{29}Si and ^{30}Si components of 2-H is, however, smaller by a factor 2.7–2.8 compared with that calculated for a diatomic molecule in the harmonic oscillator approximation. Line 2-D was broader than line 2-H, and only structure associated with ^{29}Si could be observed. The present observations demonstrate that, in GaAs:Si passivated with H or D, Si—H or Si—D bonds are formed and that the silicon atom remains bonded in the lattice.

Some epilayers were passivated in a mixture of hydrogen and deuterium in equal proportions. These samples showed the lines discussed above but no extra lines.

Silicon atoms in GaAs preferentially occupy Ga sites (Si_{Ga}) when they act as donors, but they can also occupy As sites (Si_{As}) when they act as acceptors. The concentration ratio $[Si_{As}]/[Si_{Ga}]$ in bulk Bridgman material is usually about 1/7 for total silicon doping levels up to 2×10^{18} at. cm^{-3}. At higher levels, the relative concentration of $[Si_{As}]$ increases but there is also formation of $[Si_{Ga}\text{-}Si_{As}]$ nearest-neighbor pairs and other complexes [Si-X] and [Si-Y] of unknown structure.[14] Recently similar behavior has been found in both molecular-beam epitaxy[15] (MBE) and MOCVD epitaxial layers.[16] It is necessary to determine the distribution of sites occupied by Si in the present epilayers before comments can be made on the origin of line 2. At LHeT, the localized vibrational models (LVM) of Si_{Ga}^{+} or ($Si_{Ga}^{+}As_4$) leads to a single absorption line at $\simeq$384 cm^{-1}, while the LVM absorption of Si_{As}^{-} or ($Si_{As}^{-}Ga_4$) near 399 cm^{-1} is the superposition of the LVM's of Si_{As} surrounded by the different isotope combinations (^{69}Ga: 60%, ^{71}Ga: 40%) of four Ga atoms.[14] As a calibration relating the integrated absorption of the line at 384 cm^{-1} to the Si_{Ga} concentration has been established,[17] it was possible to determine this concentration spectroscopically. The unpassivated sample with $n \simeq 4\times10^{18}$ cm^{-3} was irradiated at room temperature by 2-MeV electrons to a dose of 2×10^{18} cm^{-2} to remove the free-carrier absorption by the introduction of intrinsic defects which act as electron traps. Previous experiments involving higher doses of irradiation show that there is a negligible redistribution of silicon among the various sites that can be occupied.[18] Ratios of the spectra of the present samples with those of undoped si samples were used to calculate the impurity-induced absorption spectra. The line at 384 cm^{-1} in the spectrum of the irradiated sample (Fig. 4) reveals the presence of Si_{Ga} in a concentration of about 3×10^{18} at. cm^{-3} as deduced from the strength of the line. No other features associated with the silicon dopant were detected. The lines at 372 and 388 cm^{-1} are due to (B_{Ga}-As_i) centers produced in the si substrate by the electron irradiation.[19] We conclude from these measurements that the concentration of $[Si_{As}]$ in the epilayer was less than 5×10^{17} at. cm^{-3}. However, a concentration close to this value is expected on the basis of measurements made on other samples with a similar silicon content. The greater sensitivity for detecting Si_{Ga} compared with Si_{As}, implicit in our statements, arises because the width of the former line is only 0.3 cm^{-1}, whereas that from the latter center is about 1 cm^{-1}. Photoluminescence measurements of the donor-acceptor pairs on epilayers similar to those used here revealed only the presence of the carbon acceptor,[20] again indicating a small Si_{As} concentration, as expected with a material prepared in an excess of As vapor.

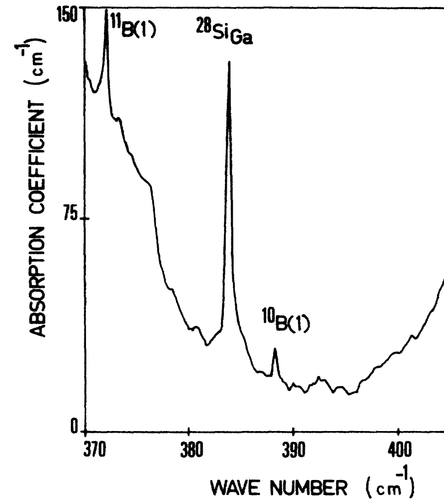

FIG. 4. Absorption spectrum at liquid-helium temperature of a 4-μm-thick GaAs:Si epilayer deposited on a si substrate showing the LVM feature due to Si_{Ga}^{+}. The silicon concentration as deduced from the strength of this line is 3×10^{18} at./cm^3. This sample was polished to a wedge shape (2°–3°) to reduce interference fringes and subjected to a dose of 2×10^{18} (2 MeV) electrons cm^{-2} to remove free carriers.

LVM measurements performed on the H- and D-passivated samples (Fig. 4) showed only a weak line from Si_{Ga} with an estimated concentration close to 10^{17} cm^{-3} in agreement with Hall data which indicated that N_D was about 3% of its initial value (Fig. 5). In the hydrogen-

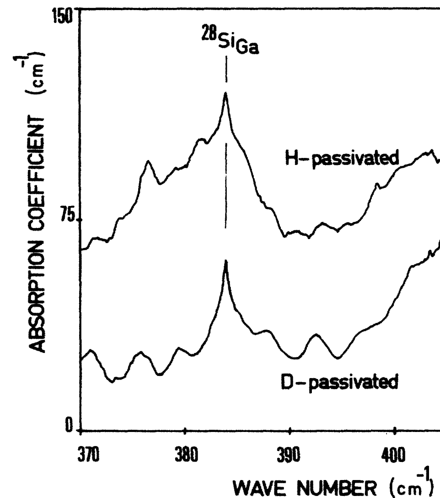

FIG. 5. Absorption spectra of the same samples as those of Fig. 2 showing the reduction in the strength of the $^{28}Si_{Ga}^{+}$ concentration from 3×10^{18} at. cm^{-3} (Fig. 4) to about 10^{17} at. cm^{-3} as a result of hydrogen or deuterium passivation. These samples were also polished to a wedge shape and differences in the background are due to a slight thickness mismatch with the undoped reference sample.

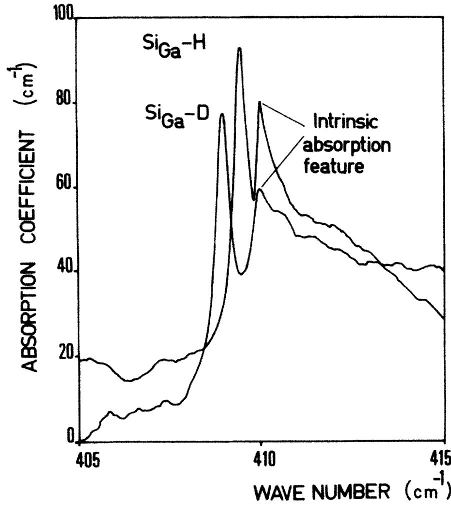

FIG. 6. Absorption spectra of the passivated samples showing the LVM features due to the vibrations of the paired silicon atoms in the $^{28}Si_{Ga}$-H and $^{28}Si_{Ga}$-D defects.

passivated sample, a previously unreported line was detected at 409.95 cm^{-1}; in the deuterated sample, the energy was reduced to 409.45 cm^{-1} (Fig. 6). The FWHP of these lines was 0.4 cm^{-1}, showing that the vibrating Si atom had arsenic (^{75}As 100% abundant) neighbors rather than gallium neighbors. Thus the mode was due to a Si_{Ga}-H pair defect. For a center with C_{3v} point-group symmetry a second line was expected but not detected in the spectral region 350–650 cm^{-1}

EPR measurements were carried out on a passivated sample at temperatures in the range 4.2–20 K using a Varian E-line X-band spectrometer, but no resonances due to dangling bonds or hydrogen were detected.

III. DISCUSSION AND MODELS

We start with a GaAs epilayer containing Si in Ga sites of tetrahedral symmetry. Diffusing hydrogen atoms are trapped at preferred locations. The isotopic structure revealed in lines 2-H and 2-D shows that one location is immediately adjacent to a silicon atom. Since a pair defect is formed, the symmetry must be lower than tetrahedral and it follows that more than one vibrational mode of the paired hydrogen is to be expected. For a defect with axial symmetry, two modes should occur: $\omega_{\parallel}$ would be a longitudinal (stretching) mode along the axis and $\omega_{\perp}$ would be a doubly degenerate (bending) mode perpendicular to the axis.

It is first postulated that hydrogen is in an interstitial site (along an anti-bonding orbital) bonded to a pentavalent silicon. The defect would have C_{3v} symmetry and the donor activity of the Si_{Ga} would almost certainly be removed (Fig. 5). The two electrons in the Si_{Ga}—H bond would have originated from the hydrogen atom and the donor electron from the silicon. The mode $\omega_{\parallel}$ would be expected to have a frequency close to that for Si-H stretch, which is normally near 2200 cm^{-1}.[11] The observed mode at 1717 cm^{-1} has a lower frequency, but it is nevertheless ascribed to this mode: The charges present on Si^{+}-H^{-} may lead to the reduction of the frequency. The hydrogen would not be bonded to any other atom but nevertheless would still be constrained to vibrate within an interstitial cage adjacent to the Si_{Ga} atom. A lower force constant would be appropriate and as a result we can associate the line 1-H with the doubly degenerate mode $\omega_{\perp}$.

This model bears similarity with those compared by Johnson *et al*[21] to explain the incomplete passivation of P donors in silicon as they also involve the binding of a H atom to already tetracoordinated P or Si atoms. Their stability calculation however showed that the binding to a P nearest-neighbor Si atom was energetically more favorable. Here, we have direct spectroscopic evidence that in GaAs:Si, H is bonded to the Si *donor* atom. We now examine this model more quantitatively and comment on alternative models.

If the perturbation of the interstitial hydrogen was small, the infrared absorption arising from the transverse mode would be expected to be double that of the longitudinal mode. However, the separation of $\omega_{\parallel}$ from $\omega_{\perp}$ indicates a strong anisotropy, and some deviations from a factor of two would not be unexpected. The total integrated absorption due to the presence of an impurity may be written[22]

$$\int \alpha(\nu)d\nu=(\pi[\mathrm{D}]\eta^2)/(nc^2M) \ , \tag{1}$$

where α is the absorption coefficient (cm^{-1}) as a function of wave number ν, and the integration extends over all lines arising from modes involving large displacements of the light impurity atom of mass M. n is the refractive index of GaAs ($n=3.57$). c is the velocity of light. [D] is the concentration of the impurity in the configuration giving rise to the lines and η is called an apparent charge (dipole moment per unit displacement) and is expected to have a value equal to the electron charge e multiplied by a factor of the order of unity.[22] We now assume that the concentration of Si_{Ga}-H centers is equal to the concentration of isolated Si_{Ga} lost as a result of the passivation treatment, i.e., about 3×10^{18} cm^{-3}. In our sample, the integrated absorption in lines 1-H and 2-H were 290 cm^{-2} and 100 cm^{-2}, respectively. The total absorption of 390 cm^{-2} would yield a value of $\eta=0.98e$. For the deuterated center the strength of lines 1-D and 2-D were 120 and 40 cm^{-2}, respectively, in agreement with the ratio found for the strengths of the hydrogen lines. The total absorption of 160 cm^{-2} leads to a value of $\eta=0.89e$, which is lower than the value determined from the absorption in the hydrogen lines. A somewhat smaller value is expected because Eq. (1) should include the absorption that will occur in the continuum below the Raman frequency.[22] However, the H and D modes are of such a high frequency that the correction factor would be only a few percent.

Measurements of the vibrational frequencies are extremely accurate so that correspondingly accurate values of the ratios r_1 and $r_2=\nu(2\text{-H})/\nu(2\text{-D})$ can be determined. The value would be exactly $\sqrt{2}$ if the hydrogen atom vibrated in a rigid well, but if it is bonded to a substitution-

al atom of the lattice that has nonzero displacements in the mode it is necessary to use a reduced mass, and r will have a smaller value. The measured values of $r_1=1.398$ and $r_2=1.376$ are significantly different and support the view that lines 2-H and 2-D are the longitudinal modes of Si_{Ga}-H and Si_{Ga}-D, respectively. It has already been stated that the experimentally isotopic splittings of the 2-H line due to the presence of ^{29}Si and ^{30}Si are too small by a factor of 2.7–2.8 as compared with the estimated values. In fact it has been found necessary[23] to scale down such estimates by about this factor for other defect complexes, such as Si_{Ga}-Ge_{As} in GaAs. The implication is that the silicon atom is still bonded to the lattice and its displacements lead to displacements of its near neighbors. In the transverse mode of the H atom there would be only small displacements of the silicon atom arising from bond bending forces and the low-energy asymmetry of the shape of lines 1-H and 1-D can be partly explained by a weak Si isotope effect. It must be pointed out that the increase of r for the $\omega_\perp$ mode is a "solid state" effect. For this mode, the restoring force is due in part to the angle bending force of the hydrogen bond together with repulsive forces from the neighboring atoms in the crystal. By contrast, for molecules with C_{3v} symmetry such as $CHCl_3$ and $CDCl_3$ the latter contribution to the restoring force is absent and the value of r for the H bending mode is essentially the same as that for the stretching mode.[24] Consequently the value of r_1 is similar to the ratio of ω_H/ω_D measured for various complexes involving H^- ions.[22]

The widths of the lines 1-D and 2-D are about double those of lines 1-H and 2-H, respectively. The model where the H atom is bound to an already tetravalent Si_{Ga} atom implies that the neutralizing atom is located close to a tetrahedral interstitial site with a Si_{Ga} nearest neighbor. As a consequence, the other three nearest neighbors will be gallium atoms and part of the increase in the linewidth will be due to the larger amplitudes of vibration of lattice atoms for the deuterium modes. The effect would arise because of the presence of mixed gallium isotopes. For example, the overall width of the fine structure due to such interactions around a boron impurity has been measured to be greater for $^{11}B_{As}$ ($\Delta=0.65$ cm^{-1}) compared with $^{10}B_{As}$ ($\Delta=0.61$ cm^{-1}).[25,26] A larger effect could be expected for hydrogen vibrations when the mass is changed from 1 to 2 amu. It follows that the line shape of 2-D should be different from that of 2-H making relative estimates of the integrated absorption somewhat imprecise, and such an effect could in principle lead to errors in estimates of η as discussed above.

The presence of the hydrogen atom next to the Si_{Ga} impurity would modify the force constants for the vibration of the donor atom. The symmetry would again be C_{3v} and so two new modes, one nondegenerate and one doubly degenerate would be produced. We have no means of estimating the apparent charge for the modified modes and neither can we predict the new frequencies. It has already been pointed out that the line due to isolated Si_{Ga}^+ donors at 384 cm^{-1} lies in a "trough" of the background two-phonon absorption, making its observation relatively easy. Lines shifted to either side by only some tens of wave numbers would occur on sloping backgrounds and would be difficult to detect. In fact one mode at 409.95 cm^{-1} has been observed with a width of only 0.4 cm^{-1}, showing that the atom involved in this mode has arsenic nearest neighbors. The presence of paired H or D was confirmed by a small isotope shift. The measured strength of the line (18 cm^{-2}) was independent of whether H or D was used to passivate the sample, showing that it corresponded to a Si mode rather than a H or D mode. The strength was only 37% of that of the original LVM line (49 cm^{-2}) from unperturbed Si_{Ga}, indicating either a reduction in the value of η when pairing occurs or more probably that the second line from the perturbed Si_{Ga} has not yet been detected.

The model discussed above cannot be regarded as established and we should therefore consider alternatives.

(a) In an earlier paper[5] it was suggested that line 1 and the neutralization of the Si_{Ga} donor could be explained by assuming that a hydrogen atom was located in an interstitial site and bonded to an As nearest neighbor to a Si_{Ga} atom. This model was proposed before the observation of line 2. Since the latter line shows silicon isotope splitting it must originate from a hydrogen atom bonded to a silicon atom, which could in principle be either Si_{Ga} or Si_{As}. The available evidence indicates that lines 1 and 2 are always observed with the same ratio of strengths[27] and it is inferred that they arise from a common defect. In that case, the earlier proposal seems unlikely. The present results demonstrate that the pair defect must be Si_{Ga}-H, as the LVM absorption from isolated Si_{Ga} atoms is removed by the presence of hydrogen in the crystal. Furthermore the concentration of Si_{As} acceptors was found to be much smaller (undetectable) that that of Si_{Ga} in unpassivated material.

(b) It is possible that during the passivation treatment, a Si_{Ga}—As bond is broken, leaving two dangling bonds. A hydrogen atom can then saturate the Si_{Ga}^+ bond and occupy an interstitial site midway between the Si_{Ga} and As atoms. The Si_{Ga} remains tetravalent and the stretching mode of Si_{Ga}-H could be attributed to the line 2-H. The lowering of the frequency from that normally found for such pairs[28] could still be explained by the presence of static charges as discussed above. The donor electron from the silicon might then combine with an electron of the adjacent As atom which has only three bonds. This proposal could convert the strained sp^3 bonding into a p orbital, leaving a structure which is reasonably stable in the chemistry of arsenic. Line 1-H is still attributed to the doubly-degenerate transverse mode of the Si_{Ga}—H bond.

(c) Rebonding of a broken Si_{Ga}—H bond might occur by the incorporation of two adjacent hydrogen atoms, one bonded to the Si_{Ga} atom and the other to the As atom. As the sum of the Si—H and As—H bond lengths is slightly greater than a Ga—As bond length it seems unlikely that the two hydrogen atoms could be accommodated along a single bond, and irrespective of the location of the hydrogen atoms, the donor activity of the Si_{Ga} would not appear to be neutralized. Secondly, no additional LVM lines were observed in samples passivated

with mixtures of hydrogen and deuterium, in contrast to the observations of Bai et al.[11] for hydrogen and/or deuterium in silicon. This model would not appear to be tenable.

(d) Electrical measurements made on the present samples indicated that the Si_{Ga} donors were partially compensated electrically by unknown acceptors which could well have been intrinsic defects. It might have been argued that line 2 arises from Si_{Ga}-H pairs, while line 1 is due to hydrogen paired with one of these acceptor centers. However, proton and deuteron implantation treatments of si GaAs lead to the production of absorption lines[29] in the spectral region near 1771 and 1238 cm^{-1}, respectively, and in principle could correspond to line 2 observed in the present work but not with line 1. However, it has been demonstrated from isotope effect that line 2 arises from a Si-H pair and so there is no evidence for hydrogen paired with intrinsic defects in our samples. Absorption near 1771 cm^{-1} in proton-irradiated si GaAs cannot be due to Si-H pairs, as it is unlikely that contemporary si GaAs will be contaminated with silicon at a level greater than 10^{15} at. cm^{-3}.

IV. CONCLUSIONS

We have shown that interstitial hydrogen atoms bond directly to Si_{Ga} atoms in *n*-type GaAs:Si. The formation of a Si—H bond on a pentavalent silicon atom is considered the most likely mechanism. This model leads automatically to the neutralization of the donor activity of the Si_{Ga} atom and it is essentially the same as that proposed for the partial passivation of phosphorus in silicon.[21] However, the alternative possibility that Si_{Ga}—As bonds are broken with the subsequent formation of Si_{Ga}—H bonds cannot be discarded. Either type of defect would have trigonal C_{3v} symmetry. Two vibrational modes of the Si-H are expected and two modes are indeed observed, one of which is ascribed to the longitudinal vibration because silicon isotope effects are detected. The transverse mode is at a much lower frequency but has 3 times the integrated intensity of the former, as might be expected. The LVM absorption from Si_{Ga}^{+} at 384 cm^{-1} is nearly all lost after the passivation treatment but only one new perturbed Si_{Ga} mode has been found. The concentration of Si-H defects was estimated from the loss of Si_{Ga} and we were able to determine an apparent charge $\eta=0.98e$ for the H modes; a lower value of $\eta=0.89e$ was determined from the D modes, but this discrepancy is not considered to be a serious shortcoming to our analysis. The average value is significantly lower than those of $\eta=1.9-2.9e$ deduced by Stavola et al.[12] for Si-H modes in silicon where the hydrogen atom was located adjacent to either an aluminum or a gallium atom.

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