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The infrared vibrational absorption spectrum of the Si–*X* defect present in heavily Si doped GaAs

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Heavily silicon doped GaAs grown by molecular beam epitaxy using a single gallium isotope source (^{69}Ga) has been studied by infrared absorption to reveal localized vibrational modes (LVMs) of Si complexes. The structure observed close to 367 cm^{-1} is the same as that present in normal GaAs:Si spectra and does not result from mixed Ga isotopes. The electron trap Si–*X* gives three LVMs at 368.4, 370.0, and 399.6 cm^{-1}, typical of second neighbor donor-acceptor pairs, but inconsistent with a previous proposal that its structure is the planar defect V_{Ga}–Si_{As}–As_{Ga}. It is now suggested that the defect is a perturbed Si_{Ga}–V_{Ga} center, involving a second Si atom or a second vacancy. © *1997 American Institute of Physics.* [S0021-8979(97)03113-7]

I. INTRODUCTION

Silicon is the preferred *n*-type dopant in GaAs but the behavior of these impurity atoms when present in a high concentration is still incompletely understood. It is known that a Si atom occupying a Ga lattice site (written as Si_{Ga}) is a shallow donor and that Si_{As} is a shallow acceptor. Doped Bridgman crystals or layers of GaAs grown by molecular beam epitaxy (MBE) on a (001) substrate are *n* type because $[Si_{Ga}]$ is greater than $[Si_{As}]$. As the total doping level $[Si]_{TOT}$ is increased, the ratio $[Si_{As}]/[Si_{Ga}]$ increases somewhat, thereby increasing the degree of compensation. Not surprisingly there is then formation of nearest neighbor Si_{Ga}–Si_{As} pairs. All three centers have been identified unambiguously in infrared (IR) localized vibrational mode (LVM) absorption spectra: the relevant frequencies are listed in Table I.[1,2] There had been problems of assignment of the line at 366.9 cm^{-1} but it is now clear that it should be attributed to the symmetric *E*-mode of the pair defect, following the correlation of its strength with two other lines of the defect at 393 and 464 cm^{-1} (see Ref. 2). We note that Si consists of three naturally occurring isotopes ^{28}Si: 92.3%, ^{29}Si: 4.7%, and ^{30}Si: 3.0%; the heavier isotopes give rise to weak LVMs on the low energy side of lines from ^{28}Si with displacements of $\sim$5 cm^{-1}/amu.[2]

It is not possible to achieve a carrier concentration greater than $n \sim 2\times10^{19}$ cm^{-3} in GaAs:Si.[3,4] The Fermi level is then located in the conduction band so that displacements are expected of Si_{Ga}^{+} donors towards interstitial sites away from nearest neighbor As atoms, leading to the formation of Si_{DX}^{-} centers.[5] Automatic self-compensation would be expected to occur, so that further increases of $[Si]_{TOT}$ should lead to a constant value of *n* once it has reached its limiting asymptotic value. Unexpectedly, *n* then *decreases* both for homogeneously doped GaAs and for δ-doped MBE layers,[3,4] where the Si atoms are confined closely to a single atomic plane. Prior to this stage, further LVM lines appear in the spectra, assigned to two defects originally designated Si–*Y* and Si–*X* (see discussion in Ref. 6). Si–*Y*, giving LVMs at 366.7, 367.5, and 397.8 cm^{-1}, has been identified with a Si_{Ga}–V_{Ga} second neighbor pair, where the Ga vacancy (V_{Ga}) is expected to trap at least two electrons.[7] The defect has been observed in Bridgman samples, annealed in the range $550 \leqslant T \leqslant 800$ °C following prior plastic deformation,[8] and also in (001) MBE samples grown at 200 or 250 °C under As-rich conditions.[9,10] The latter measurements were invaluable as the three sharp absorption lines were present with no interference from adjacent lines. The Si–*X* defect, believed to give LVMs only close to 369 cm^{-1}, has been attributed to a second deep electron trap with a proposed planar structure V_{Ga}–Si_{As}–As_{Ga}, generated by two local atomic jumps within a Si_{Ga}–As–V_{Ga} defect.[2] Nevertheless, the related discussion was concluded with the remark that ''Further work is required to confirm or reject this proposal.'' Other recent work, involving both IR and Raman scattering measurements, has implied that not all of the Si atoms present give rise to detectable LVM absorption lines.[4] In effect, some Si is simply ''lost'' in uniformly doped material, although $(Si–Si)_n$ clusters, detected by Raman scattering, are found in δ layers.[11] The presence of silicon clusters has also been reported in studies using transmission electron microscopy[12] and cross-sectional scanning tunneling microscopy (XSTM).[13] This and other observations imply that Si atoms make diffusion jumps during the growth process at temperatures $T \geqslant 400$ °C (see Refs. 2 and 4).

We now present measurements made on *n*-type GaAs:Si grown on (001) substrates using ^{69}Ga as a single isotopic source, instead of natural Ga that consists of two isotopes ^{69}Ga (60% abundant) and ^{71}Ga (40% abundant). Differences in the observed structure of absorption features allow assignments to be made to Ga isotopic fine structure, but if there are no changes the assignments have to be to LVMs with nearly equal frequencies. The measurements reported here allow us to conclude that the Si–*X* defect must have a structure different from that proposed previously since a new line has been identified on the high energy side of that of Si_{As}, and structure close to 367 cm^{-1} is found not to be due to

TABLE I. Line position for Si complexes.

Center	Line position (cm^{-1})	Comments
$^{28}Si_{Ga}$	383.9	
$^{29}Si_{Ga}$	378.4	
$^{30}Si_{Ga}$	373.4	
$^{28}Si_{As}$	398.4 (center frequency)	wide line due to mixed Ga isotopes
$^{28}Si_{As}$[a]	398.9	^{69}GaAs:Si layer lies under the pair line at 393.3 cm^{-1}
$^{29}Si_{As}$		
$^{30}Si_{As}$	389	
$^{28}Si_{Ga}$–$^{28}Si_{As}$	366.9, 393.3, and 464.7	
$^{28}Si_{Ga}$–Y	366.8, 367.5, and 397.8	
Si–X[a]	368.4, 370.0, and 399.6	

[a]New results.

mixed Ga isotopes. This article updates an earlier review[2] that, in turn, updated earlier publications.[1,6] New models for the Si–X defect are suggested in Sec. IV.

II. EXPERIMENTAL DETAILS

We have re-measured the absorption spectra of (001) MBE Si-doped GaAs layers grown with a natural Ga source to a thickness of ~15 μm at the Philips Research Laboratory, Redhill, U. K. (see Ref. 14): the new spectra are significantly superior to those reported in our earlier papers. Linewidths and lineshapes of the observed LVMs were then compared with the corresponding modes found for single Ga isotope ^{69}GaAs:Si layers grown by MBE. The latter samples were grown in a VG V80H machine on semi-insulating liquid encapsulated Czochralski (001) GaAs wafers. A GaAs buffer layer was grown first with a normal Ga source and then a Si doped ^{69}GaAs layer was grown to a thickness of either 0.6 μm ($[Si]=8\times10^{18}$ cm^{-3}) or 4 μm ($[Si]=3\times10^{19}$ cm^{-3}). The growth rate was 0.5 $\mu m\,h^{-1}$ (the beam equivalent pressures of ^{69}Ga and As were 2.0×10^{-7} and 1.6×10^{-5} mbar, respectively) and the temperature was maintained at 580 °C throughout the growth. Analysis of the metal source indicated that ^{69}Ga had an abundance of 99.7%: some metallic impurities were just detected with maximum concentrations of 0.005%.

IR absorption measurements were also made on GaAs:Si layers grown by liquid phase epitaxy (LPE). It was important to determine the frequency and profile of the weak symmetric E-mode of Si_{Ga}–Si_{As} pairs at ~366.9 cm^{-1} (Table I) since there are no adjacent absorption lines close to this frequency in LPE layers.

Spectra were obtained using a Bruker IFS 120 HR interferometer operated at a resolution of 0.1 cm^{-1} with the samples held at ~10 K. The substrates of all samples were wedged to eliminate interference fringes in recorded spectra. Prior to these measurements, doped samples were subjected to 2 MeV electron irradiation at room temperature to eliminate free-carrier absorption. Apart from increasing the transmission, an additional advantage is that LVMs no longer show derivative-shaped Fano profiles.[15,16] Finally, scaled absorption spectra from undoped samples were used to subtract

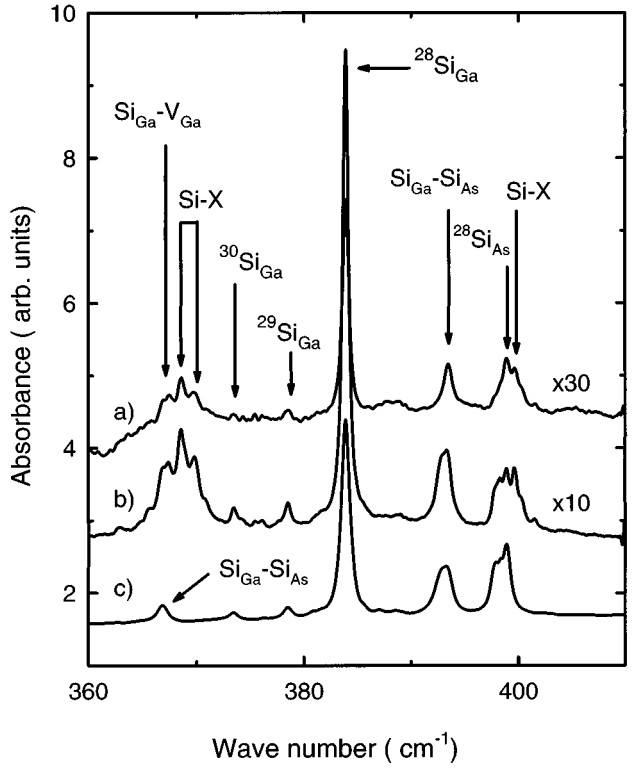

FIG. 1. Spectra showing LVMs from the principal silicon defects in as-grown n-type GaAs following 2 MeV electron irradiation to remove free-carrier absorption: (a) ^{69}GaAs:Si grown by MBE. (b) A similar sample to (a) but using a natural Ga source. (c) A similar sample grown by LPE that does not show the Si–X or Si_{Ga}–V_{Ga} complexes.

intrinsic two-phonon features from the spectra of the doped samples.

III. INFRARED SPECTRA

The spectra of highly doped (001) MBE samples grown using ^{69}Ga and natural Ga [Fig. 1, traces (a) and (b)] show strong LVM lines from Si_{Ga}, Si_{Ga}–Si_{As} pairs and Si_{As}, together with structure in the spectral range 365–370 cm^{-1}, including that from Si–X. GaAs:Si grown by LPE shows the same modes except that there is no detectable absorption from Si–X [Fig. 1, trace (c)]. The frequencies of $^{28}Si_{Ga}$, $^{29}Si_{Ga}$, and $^{30}Si_{Ga}$ are within the measurement errors, the same for all samples (Table I), consistent with previous cluster calculations that demonstrate that the vibrational displacements of second neighbor Ga atoms are negligible for these modes.[17] Difference spectra for the two types of MBE sample, after subtraction of a scaled spectrum from an LPE layer, are shown in Fig. 2. The subtraction procedure leads to an almost complete removal of the Si_{Ga}–Si_{As} pair line at 393 cm^{-1} in the MBE sample grown with natural Ga [trace (b)] (the linewidth was slightly greater for the LPE layer). The same procedure applied to the ^{69}GaAs:Si sample leads to a residual derivative-shaped profile. The higher frequency feature of this profile is due to the modes, involving naturally occurring ^{69}Ga, that contribute to the isotopic fine-structure that is never resolved: calculated profiles of the overlapping

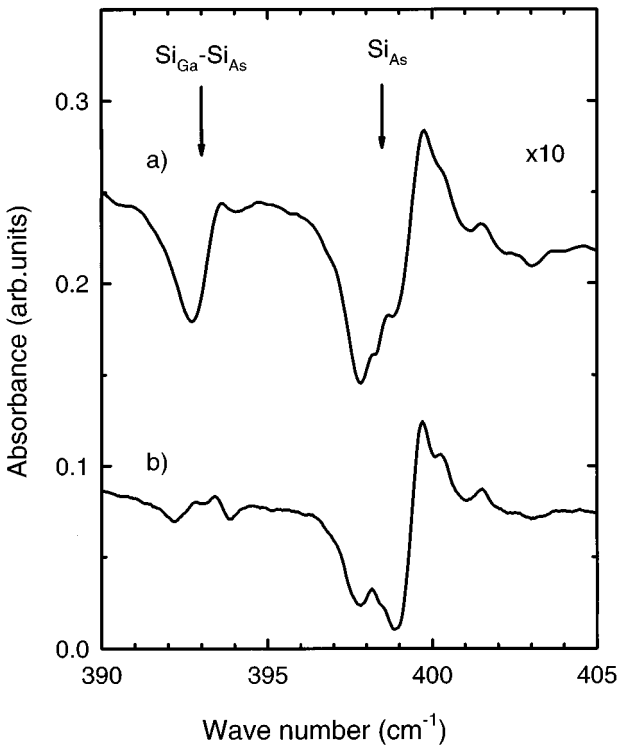

FIG. 2. Expanded difference spectra of the LVMs from Si_{Ga}–Si_{As} pairs and Si_{As} acceptors after scaling. Trace (a) is the spectrum shown in Fig. 1(a) after subtraction of spectrum 1(c); there is cancellation of the high frequency part of the line from Si_{Ga}–Si_{As} pairs related to the presence of ^{69}Ga neighbors of the Si_{As} atom but a strong dip due to the additional absorption from ^{71}Ga present in the spectrum (c); the difference structure around the Si_{As} line has a derivative structure. (b) Spectrum shown in Fig. 1(b) after subtraction of spectrum 1(c); there is essentially complete cancellation of the Si_{Ga}–Si_{As} pair line when allowance is made for small changes in the linewidth; the difference structure close to the Si_{As} LVM is similar to that shown in trace (a), showing that the highest frequency components are not due to isotopic structure.

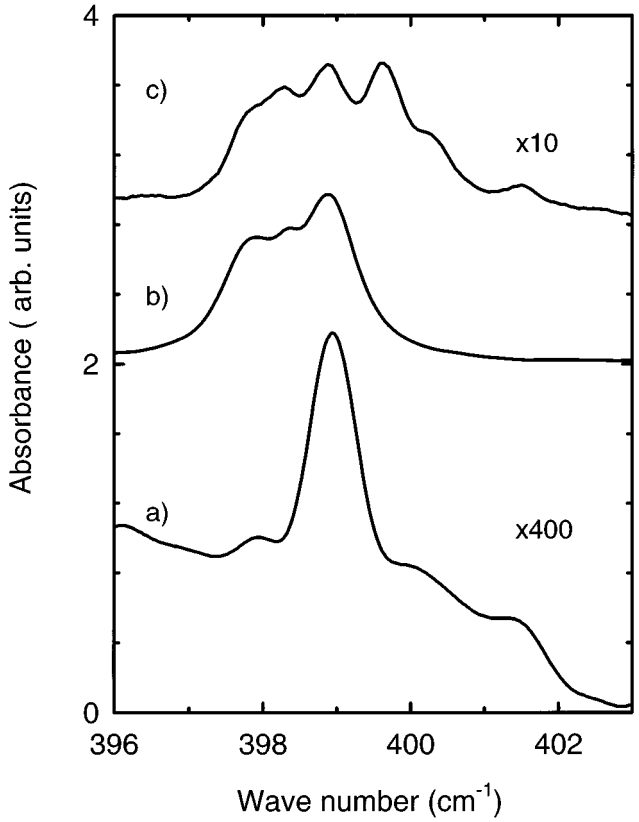

FIG. 3. (a) The absorption from the more lightly doped (001) MBE ^{69}GaAs:Si layer showing a sharp line with no isotopic fine structure from Si_{As}: (b) The absorption from Si_{As} showing partially resolved isotopic fine structure from a Si doped LPE layer. (c) Absorption due to Si_{As} in a highly doped MBE layer, together with extra absorption at higher frequencies found only in samples that show absorption from the Si–X complex.

isotopic components are discussed in Ref. 6. The dip at low frequencies is due to the absence of modes involving ^{71}Ga in the single isotope GaAs.

We next investigate the absorption at frequencies close to 399 cm^{-1} (Figs. 1 and 3). The difference spectra (Fig. 2) show similar derivative profiles for the ^{69}Ga and the natural Ga MBE samples. The spectrum of a lightly Si doped ^{69}Ga MBE layer which shows only the Si_{Ga} and Si_{As} LVMs is also included in Fig. 3. For this sample, the Si_{As} line has a full width at half maximum of $\Delta \sim 0.7$ cm^{-1}, comparable with that of the Si_{Ga} line and the line position coincides with the peak on the high energy side of the Si_{As} absorption at 398.9 cm^{-1} from the LPE sample. It follows that structure at slightly higher frequencies (Figs. 1 and 3) cannot be due to isotopic shifts of the frequency of the Si_{As} LVM because ^{69}Ga is the lighter Ga isotope and ^{28}Si is the lightest Si impurity isotope. This structure is only detected in samples showing absorption from Si–X, close to 368 cm^{-1}. This conclusion could have been reached without using ^{69}Ga samples but has not been recognized previously.

Expanded spectra in the region of 367 cm^{-1} (Fig. 4) corresponds to the three spectra shown in Fig. 1. The vertical lines demonstrate that the frequencies of the various features in the spectra of the ^{69}Ga and the natural Ga samples are the same. It is concluded that none of this structure arises from the presence of mixed Ga isotopes. The overlapping lines must arise from more than one type of center since at least five modes are resolved. We note that the linewidth of each of the various components is essentially the same as those of the lines due to isolated Si_{Ga} donors that can be seen most easily for the $^{30}Si_{Ga}$ mode at 373 cm^{-1} (Fig. 4). It is inferred that the Si atoms in the complexes occupy Ga rather than As lattice sites. The absorption from the pair line at 366.9 cm^{-1} was then subtracted from the composite absorption: the appropriate strengths of the line were calculated from the measured strength of the well resolved 393 cm^{-1} line (Table I). The residual absorption comprises four main peaks, together with some weaker features (Fig. 4). Two of the stronger lines at 366.7 and 367.5 cm^{-1} are due to the Si_{Ga}–V_{Ga} defect (Table I), leaving two other strong lines at 368.6 and 369.7 cm^{-1}, that we now assign to Si–X. It is implied from the argument above that a Si_{Ga} atom is incorporated in the latter defect.

IV. DISCUSSION

The most important new conclusion resulting from this work is that the measured structure of the absorption close to 367 cm^{-1} is not due to the presence of mixed ^{69}Ga and

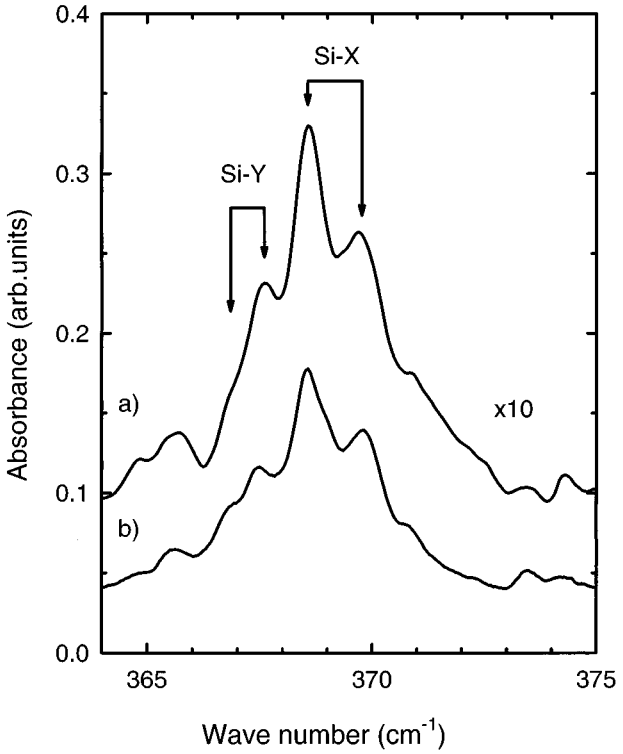

FIG. 4. Absorption in the region of Si–X after subtraction of the absorption from Si_{Ga}–Si_{As} pairs at 366.9 cm^{-1}, shown in Fig. 1(c). Difference spectra (a) and (b) for MBE GaAs:Si grown using ^{69}Ga and natural Ga, respectively, show essentially the same features that cannot be due to isotopic fine structure. Two weak lines coincide with the frequencies of the two low frequency modes of Si_{Ga}–V_{Ga} pairs, leaving two other resolved modes that we assign to the Si–X defect. The similar widths of these lines to those of Si_{Ga}–V_{Ga} implies that the Si atom has As neighbors (cf. the line from $^{30}Si_{Ga}$ in Fig. 1).

^{71}Ga isotopes. It is therefore not surprising that the linewidths of the individual components correspond to those of vibrational modes of isolated Si_{Ga} donors. It follows that the components are due to complexed Si_{Ga} atoms. In addition, structure on the high energy side of the absorption close to 399 cm^{-1}, is observed only when absorption from Si–X is present. It is implied that the Si–X defect that acts as a deep electron trap gives rise to three LVMs at 368.4, 370.0, and 399.6 cm^{-1}, respectively, rather than only low frequency modes[2] close to 367 cm^{-1}. Our previous speculative proposal for the structure of the Si–X defect cannot be correct since a Si_{As} acceptor is not present and it is necessary to consider different atomic arrangements.

The disposition of the LVMs from Si–X are similar to those reported for various second neighbor Si-acceptor pairs, including Si_{Ga}–Zn_{Ga},[18] Si_{Ga}–Cu_{Ga},[19] and Si_{Ga}–V_{Ga} [9,10] (Table I). The structures of the known pairs have been analyzed by *ab initio* local density functional theory[20] and it was shown that Zn and Cu acceptors move away from the Si_{Ga} donor, in spite of the Coulombic attraction. Such displacements lead to gallium vacancy-like centers (partial vacancy) that have stronger interactions with the Si_{Ga} atom. For each type of center, two relatively close LVMs occur around 370 cm^{-1} and a third mode occurs at a much higher frequency ~400 cm^{-1}, leading to broad agreement with measured LVM frequencies. A comparison with the data for the Si–X defect implies that it is also a Si_{Ga} atom paired with a second neighbor acceptor, complementing the conclusion resulting from measured linewidths. The acceptor would have to be a vacancy or an unidentified metal atom. It is now necessary to review other evidence that helps resolve this ambiguity.

We note first that recent positron annihilation measurements[21] indicate the presence of negatively charged V_{Ga} vacancies in highly Si doped GaAs but no information is obtained from such measurements relating to pairing. Second, the Si–X center has never been reported in n-type LPE GaAs (grown at relatively low temperatures) even when the Si doping levels are high. It is unlikely that a high concentration of V_{Ga} defects would be introduced because of the high Ga supersaturation. Since any heavy metals that might be present as contaminants would be expected to segregate into the liquid Ga, their incorporation into the growing GaAs would be inhibited. The low temperature transition (~300–350 °C) of Si–Y to Si–X in MBE GaAs (grown at 200 or 250 °C and then annealed in the MBE equipment) would also argue against the involvement of transition metals. Finally, it is recalled that compensation of heavily Si doped Bridgman crystals by the in-diffusion of Cu at a temperature in the range 850–950 °C leads to the removal of grown-in Si–X and Si–Y (Si_{Ga}–V_{Ga}) centers with the formation of Si_{Ga}–Cu_{Ga} second neighbor pairs.[19] These changes are simply explained since diffusing interstitial Cu atoms would be trapped by V_{Ga} defects incorporated as Si_{Ga}–V_{Ga} pairs. The simultaneous loss of Si–X then provides evidence that this defect also incorporates a V_{Ga}. In summary, there is no evidence that the Si–X contains a metal atom.

The Si–X defect has to be identified with a Si_{Ga}–V_{Ga} center with a second adjacent Si impurity or another lattice defect that perturbs the V_{Ga}, if Si_{Ga}–Y is assigned to a Si_{Ga}–V_{Ga}. It is only this proposed perturbation that would distinguish the two centers and it is therefore possible to interchange the two assignments. We now consider briefly possibly ways in which perturbations could arise. It has been pointed out that some Si atoms do not occupy substitutional sites in MBE material with very high carrier concentrations even when it is grown at temperatures as low as ~350 °C.[4] During anneals at higher temperatures there are redistributions of Si atoms among the various sites[2,22,23] (see also Ref. 10). We have speculated that Si^{+}_{Ga}–Si^{+}_{DX} pairs might dissociate leaving a Si atom in an interstitial site adjacent to a vacancy. In that case, the displaced Si_{Ga} atom could perturb the resulting vacancy. However, the possibility that a second vacancy is involved cannot be ruled out.

The results and discussion presented here are complemented by recent observations made by XSTM[24] that have been interpreted in terms of Si_{Ga}, Si_{As}, Si_{Ga}–Si_{As} pairs, Si_{Ga}–V_{Ga} and $(Si)_n$ clusters in bulk GaAs grown by the gradient freeze method. The observation of $(Si)_n$ clusters has not been reproduced in the present IR study and it may be implied that such clusters occupy interstitial rather than substitutional sites. The XSTM data do not appear to discriminate between the Si–X and Si–Y defects. A sensible way forward at this stage would be to carry out traditional IR absorption measurements and XSTM studies on common

samples but it is essential to recognize that the two techniques are both spectroscopic in nature, although in different ways, and as a consequence adequate cross-referencing of interpretations is essential.

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