Aligned defect complex containing carbon and hydrogen in as-grown GaAs epitaxial layers

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A hydrogen-stretching vibration at 2688 cm^{-1}, previously observed in heavily-carbon-doped GaAs grown by metal-organic molecular-beam epitaxy and assigned to a defect complex that contains carbon and hydrogen, has been studied by infrared-absorption spectroscopy. The absorption at 2688 cm^{-1} has been found to be preferentially polarized along a particular $\langle 110 \rangle$ axis in the (001) growth plane. We propose that this band is due to a complex that is aligned at the growth surface and then maintains its alignment as the crystal is grown. The annealing of the 2688-cm^{-1} band and its alignment have been examined. We also find that the 2688-cm^{-1} complex can be formed by annealing heavily-carbon-doped GaAs between 500 and 650 °C in the presence of hydrogen. These results provide insight into the interactions of carbon and hydrogen in heavily-carbon-doped GaAs and lead us to tentatively assign the 2688-cm^{-1} band to a $(C_{As})_2H$ complex. We suggest that the annealing of this center and of its alignment is due to the dissociation and reassociation of C_{As} pairs that are controlled by the presence of hydrogen.

I. INTRODUCTION

Carbon has become an attractive *p*-type dopant for epitaxial GaAs and related alloys because it has a low diffusivity[1–5] and can be incorporated at concentrations greater than 10^{20} cm^{-3} during growth by metal-organic molecular-beam epitaxy (MOMBE) (Refs. 5–9) or metal-organic chemical vapor deposition (MOCVD).[10–13] For example, during the growth of GaAs by MOMBE from trimethylgallium (TMG) and arsine, the carbon is introduced via the surface decomposition of the TMG. Carbon occupies an arsenic sublattice site C_{As} in GaAs where it is an acceptor. Hydrogen also can be readily incorporated into heavily-carbon-doped GaAs epitaxial layers and related alloys during crystal growth[14–29] as an unintentional contaminant from a variety of possible sources that include the metalorganics AsH_3 and H_2. Hydrogen can also be introduced during post-growth annealing in H_2 or arsine.[18,19,25,28–31] It is well known that hydrogen forms stable neutral complexes with carbon and thereby reduces the active acceptor concentration in heavily-C-doped GaAs layers.

The H-stretching vibrations of complexes that contain carbon and hydrogen in GaAs have been studied previously by infrared (IR) (Refs. 15, 18–21, 23, and 30–33) and Raman[21,22] spectroscopy, and provide an excellent probe of the concentrations and characteristics of the C-H centers. Clerjaud *et al.*[32] first assigned the IR-absorption band at 2635 cm^{-1} to the C_{As}-H complex with H near the bond center between the C_{As} acceptor and a Ga nearest neighbor. For heavily-carbon-doped GaAs grown by MOMBE, H-stretching features for as-grown samples have been observed at 2636, 2643, 2651, and 2688 cm^{-1} (Refs. 15, 18, 19, and 29). For heavily-carbon-doped GaAs samples grown by MOCVD, the band at 2636 cm^{-1} dominates the spectrum,[18–23,29] although weak features at 2643 and 2651 cm^{-1} are sometimes observed.[19,29] The band at 2636 cm^{-1} was assigned to C_{As}-H, following Clerjaud *et al.*[32] The bands at 2643, 2651, and 2688 cm^{-1} have also been assigned to complexes that contain carbon and hydrogen, but their structures are unknown.[15,18,19,29]

In this paper, we report that the 2688-cm^{-1} band observed in heavily-C-doped GaAs grown by MOMBE is strongly polarized along a particular $\langle 110 \rangle$ direction in the (100) growth plane. This is an unexpected result because the different $\langle 110 \rangle$ directions are crystallographically equivalent. Our results give clues as to the microscopic structure of the defect complex that gives rise to this absorption band. We have investigated the decay of the polarization of the 2688-cm^{-1} band upon annealing. The annealing results allow us to propose a mechanism for the reorientation of the aligned complex and provide interesting information about the interactions of carbon and hydrogen. In this paper we show that the presence of H in the annealing ambient can effect the carbon reactions that occur for annealing in the range of temperatures between roughly 500 and 700 °C.

Unusual polarization effects have been observed previously in luminescence experiments performed on GaAs epitaxial layers grown by molecular-beam epitaxy (MBE).[34,35] In this case, the luminescence of a family of bands first reported by Künzel and Ploog[36,37] was discovered to be strongly polarized along a particular $\langle 110 \rangle$ direction in the (001) growth plane.[38,39] The polarized luminescence has been assigned to bound exciton recombination at pair defects which have been incorporated during growth, with their main symmetry axis along a particular $\langle 110 \rangle$ direction.[34,35] The chemical identity of the defect complexes is unknown. (There is also another family of lines that arises from a defect complex whose main symmetry axis is along a particular

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⟨111⟩ direction.[35]) We will present evidence in this paper that the polarized absorption spectra we have observed in heavily-C-doped GaAs are not due to the same defects observed in the luminescence spectra. However, the polarization effects observed in our absorption experiments and the previous luminescence experiments both involve defect alignment along a preferred ⟨110⟩ direction in the (001) growth plane, and the mechanism for the defect alignment during growth for our samples is likely to be similar to that proposed by Skolnick *et al.*[39]

II. EXPERIMENTAL PROCEDURES

We have examined several heavily-carbon-doped GaAs epitaxial layers that were grown by MOMBE or MOCVD on semi-insulating GaAs substrates. MOMBE growth was performed in a Varian gas-source Gen II MOMBE system with arsine (AsH_3) and trimethylgallium [$(CH_3)_3Ga$)] source gases and He carrier gas.[40] The arsine gas was introduced through a low-pressure Varian cracker to decompose the hydride. The growth temperature was 500 °C as monitored by the substrate thermocouple.

We examined one epitaxial layer that was grown by MOCVD in a low-pressure (30 Torr), vertical geometry reactor[41] at a growth temperature of 520 °C. The source gases were TMG, introduced with H_2 carrier gas, and AsH_3. The carbon source was CCl_4, that was supplied as a 500-ppm mixture in H_2. The epilayer was cooled in AsH_3 from the growth temperature to near 450 °C (about 5 min), and the sample remained in flowing H_2 until it was cooled to near 100 °C (about 30 min) and removed from the MOCVD reactor.

The active acceptor concentration N_A in the GaAs layers was determined from Hall-effect measurements made by the Van der Pauw method with HgIn-alloyed contacts. IR-absorption spectra were measured with a Bomem DA3.16 Fourier-transform infrared spectrometer equipped with an InSb detector. All the IR-absorption measurements were made with a resolution of 2 cm^{-1} at liquid-He temperature in an Oxford CF1204 cryostat. For polarized absorption measurements, the transmitted light was polarized with a wire grid polarizer on a CaF_2 substrate that was placed after the sample.

Several samples were annealed in H_2, D_2, or He ambients following growth. These samples were sealed in quartz ampoules with $\frac{2}{3}$ atm of the annealing gas, and annealed in a muffle furnace. Following the anneal, the samples were quenched to room temperature in ethylene glycol. It has been found previously that annealing heavily-carbon-doped GaAs in H_2 at 450 °C passivates roughly 20% of the carbon acceptors in epitaxial layers with active acceptor concentrations in the mid-10^{20}-cm^{-3} range.[19,29] We have used this method for intentionally introducing H into heavily-carbon-doped epitaxial layers.

III. EXPERIMENTAL RESULTS

A. Strongly polarized absorption band at 2688 cm^{-1}

IR-absorption spectra for two GaAs:C samples that were measured with light polarized parallel to the two different ⟨110⟩ directions in the (001) growth plane are shown in Fig. 1. Both samples were grown by MOMBE from TMG and AsH_3 and have acceptor concentrations of 2×10^{20} and 5×10^{20} cm^{-3}, respectively. Absorption bands are observed at 2636, 2643, 2651, and 2688 cm^{-1}. The band at 2688 cm^{-1} is strongly polarized along a particular ⟨110⟩ direction, while the other bands have equal intensity for both polarization directions. Samples from four different wafers grown by MOMBE were examined. For all of these samples, the IR-absorption band at 2688 cm^{-1} was found to be preferentially polarized along one of the ⟨110⟩ directions for the (001) growth plane. Hence the 2688-cm^{-1} absorption band must be due to a low-symmetry defect complex that is aligned in the crystal such that the transition moment for the H-stretching vibration lies in just one of the two {110} planes that are perpendicular to the (001) growth plane. A convenient measure of the preferential polarization is the dichroism D defined as

$$D \equiv (\alpha_{1\bar{1}0} - \alpha_{110})/(\alpha_{1\bar{1}0} + \alpha_{110}) , \quad (1)$$

where the α's are the absorption coefficients at 2688 cm^{-1} for the polarization direction given by the subscript. For the sample with $N_A = 2\times10^{20}$ cm^{-3}, we have found $D = 0.85$, and for the sample with $N_A = 5\times10^{20}$ cm^{-3}, we have found $D = 0.65$. (We have arbitrarily chosen the [1$\bar{1}$0] direction to be that ⟨110⟩ polarization

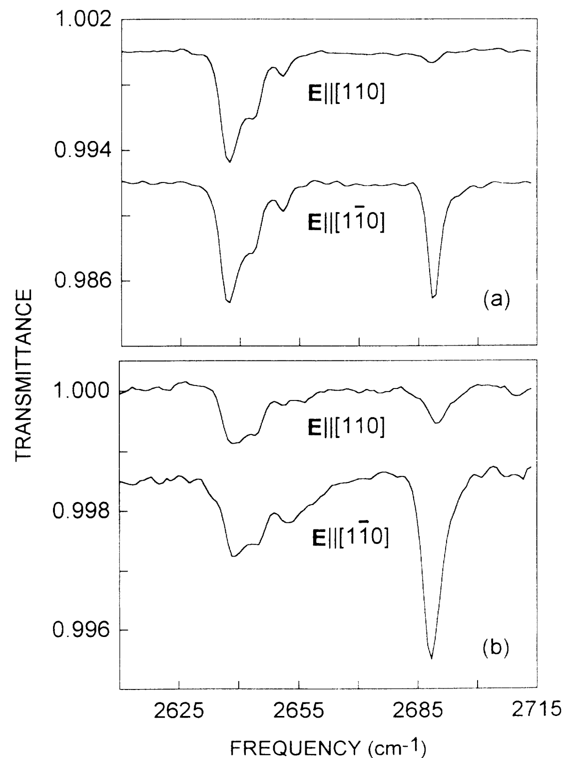


FIG. 1. IR-absorption spectra, measured near 4.2 K, are shown for heavily-carbon-doped GaAs grown by MOMBE with (a) $N_A = 2\times10^{20}$ cm^{-3}, and (b) $N_A = 5\times10^{20}$ cm^{-3}. The spectra are measured with light polarized along the [110] and [1$\bar{1}$0] directions in the (001) growth plane.

direction which shows the stronger 2688-cm^{-1} absorption band.)

We note that strain in the epitaxial layer cannot be the cause of the polarization of the 2688-cm^{-1} band. We have shown that the isolated C_{As}-H complex which gives rise to the absorption band at 2636 cm^{-1} can be aligned easily by an externally applied stress.[42] If there were residual stress in the epitaxial layer, the 2636-cm^{-1} band would also be strongly polarized and this is not observed.

It is unexpected to observe polarization effects along a particular ⟨110⟩ direction in the (001) growth plane, because these directions are crystallographically equivalent in the bulk of the epilayer. However, similar polarization effects have been observed in luminescence experiments performed on MBE-grown GaAs epitaxial layers.[34,35,38,39] For this case, Skolnick *et al.*[39] noted that the ⟨110⟩ directions are not equivalent in the zinc-blende lattice *at the growth surface*. For an As-stabilized (001) surface, all of the As-Ga bonds to the layer below the surface are in just one of the {110} planes, say the (110), whereas all of the As-Ga bonds that will be formed above the surface are in the perpendicular {110} plane, say the $(1\bar{1}0)$. Thus the two ⟨110⟩ directions are distinguished at the growth surface even though they are equivalent in the bulk. Hence, to be aligned in a particular {110} plane, defect complexes must be aligned at the growth surface and then maintain their alignment as the crystal continues to grow and the complexes are incorporated into the bulk of the layer. This mechanism for the alignment of defects during growth, proposed by Skolnick *et al.*,[39] provides a mechanism by which the defect complex we have observed can be preferentially aligned.

A MOMBE-grown sample with $N_A = 5\times10^{20}$ cm^{-3} was annealed in D_2 gas at 450 °C for 30 min. Spectra for this sample are shown in Fig. 2. The bands in the H-stretching spectrum each have a corresponding band in the D-stretching spectrum following the anneal in D_2 gas.[19,29] We find that the 2688-cm^{-1} band's deuterium-shifted counterpart at 2008 cm^{-1} is also strongly polarized along the same ⟨110⟩ axis as the corresponding H-vibration at 2688 cm^{-1}. The result that a strongly polarized D-stretching band is formed when D is diffused into the crystal following growth leads us to conclude that there is an underlying, low-symmetry defect that can bind H or D. The observed polarization of the H- or D-stretching vibrations reflects the alignment of the underlying low-symmetry defect to which the H or D becomes bound. In Sec. IV, we will propose that the underlying defect is a C_{As} pair, preferentially aligned along a particular ⟨110⟩ direction.

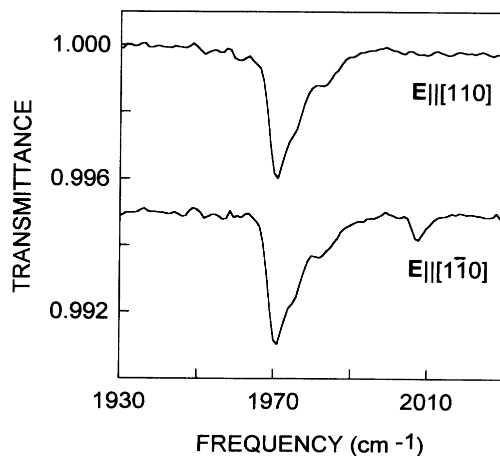


FIG. 2. IR-absorption spectra, measured near 4.2 K, are shown for heavily-carbon-doped GaAs grown by MOMBE with $N_A = 5\times10^{20}$ cm^{-3} into which deuterium was introduced following growth. The spectra are measured with light polarized along the [110] and $[1\bar{1}0]$ directions in the (001) growth plane.

B. Annealing stability of the 2688-cm^{-1} center and its alignment

We have annealed several samples from the wafer with $N_A = 5\times10^{20}$ cm^{-3} grown by MOMBE to explore the loss of alignment and dissociation of the complex that gives rise to the 2688-cm^{-1} band. One set of samples was annealed in sealed ampoules that contained $\frac{2}{3}$ atm of H_2 for 30 min. Polarized absorption spectra of samples annealed in H_2 are shown in Figs. 3(a)–3(c) (solid curves). The 2636-cm^{-1} band due to the C_{As}-H complex has a greater intensity than in the as-grown sample shown in Fig. 1(b) because of the greater degree of passivation following the anneal in hydrogen. The intensity of the 2688-cm^{-1} center is not changed by annealing in hydrogen at 520 °C. As the annealing temperature is increased, the preferential polarization of the 2688-cm^{-1} band

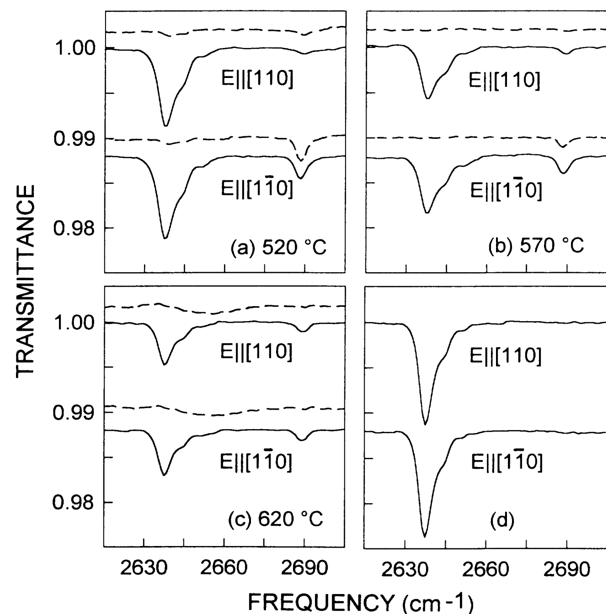


FIG. 3. IR-absorption spectra, measured near 4.2 K, are shown for heavily carbon-doped GaAs grown by MOMBE with $N_A = 5\times10^{20}$ cm^{-3}. The spectra are measured with light polarized along the [110] and $[1\bar{1}0]$ directions in the (001) growth plane. In (a)–(c), spectra are shown for samples annealed in H_2 (solid curves) or He (dashed curves) at the temperature indicated for 30 min. In (d), spectra are shown for the sample that had been annealed in He at 620 °C [spectra shown dashed in (c)], which was then subsequently annealed in H_2 at 450 °C.

disappears. Annealing in H_2 at temperatures higher than are shown in Fig. 3 causes the intensity of the 2688-cm^{-1} center (the average of both polarizations) to decrease as the center is annealed away. These data are collected in Fig. 4, where the intensity and dichroism are plotted for the 2688-cm^{-1} band as functions of the annealing temperature. (Intensity is shown normalized to the 2688-cm^{-1} intensity for the as-grown sample.) It is seen that the dichroism is annealed away at 600 °C in an H_2 ambient, and that the 2688-cm^{-1} band disappears at 700 °C.

A second set of samples, annealed in a He ambient for 30 min, gave different results than those discussed above that were annealed in H_2. Polarized absorption spectra are shown in Figs. 3(a)–3(c) (dashed curves) for samples annealed in sealed ampoules that contained $\frac{2}{3}$ atm of He. The dichroism for the 2688-cm^{-1} band does not decay. Instead the polarized 2688-cm^{-1} band is annealed away as the temperature is increased without loss of alignment. This decay of the intensity of the 2688-cm^{-1} band upon annealing in the He ambient is also plotted as a function of annealing temperature in Fig. 4. We find that the decay of the intensity of the 2688-cm^{-1} band, for samples annealed in He, closely follows the loss of alignment for samples annealed in H_2. (The C_{As}-H complex observed at 2636 cm^{-1} is not stable for any of these annealing temperatures in a He ambient.)

In many cases, the loss of alignment of a defect complex upon annealing is due to a thermally activated reorientation process which occurs while the complex maintains its integrity. However, the disappearance of the 2688-cm^{-1} band upon annealing in He closely follows the loss of alignment. This suggests that during annealing in H_2 there is a dynamic equilibrium in which the 2688-cm^{-1} complexes dissociate and reform elsewhere with random orientation.

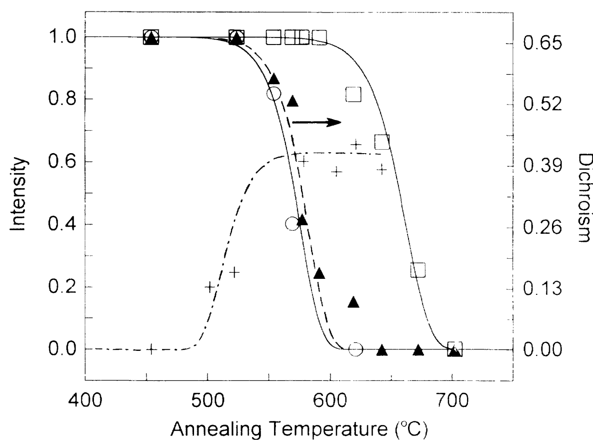


FIG. 4. Annealing data for samples from the wafer with $N_A = 5\times10^{20}$ cm^{-3}. The solid triangles and dashed curve (▲, — — —) are for the dichroism (right axis) of samples annealed in H_2. The open squares and solid curve (□, ——) are for the intensity of the 2688-cm^{-1} band (left axis) for samples annealed in H_2. The open circles and solid curve (○, ——) are for the intensity of the 2688-cm^{-1} band (left axis) for samples annealed in He. The crosses and chained curve (+, —·—·—·) are for the intensity of the 2688-cm^{-1} band (left axis) for samples that had been annealed at 620 °C in He and then subsequently annealed in H_2 at the indicated temperatures for 30 min. All of the lines shown are drawn to guide the eye.

To further explore the disappearance of the 2688-cm^{-1} band upon annealing in He, we have reintroduced hydrogen into these samples with a subsequent anneal at 450 °C in H_2 gas. Absorption spectra are shown in Fig. 3(d) for a sample that had been annealed at 620 °C in He and subsequently annealed in H_2 at 450 °C. The 2636-cm^{-1} band due to the C_{As}-H center is regenerated by the introduction of H into the sample, while the 2688-cm^{-1} band does not reappear. We conclude that the anneal in He not only causes H to dissociate from the 2688-cm^{-1} complex, but also eliminates the center to which the H was attached.

It is fortunate that the 2688-cm^{-1} center is aligned following growth by MOMBE. The temperature where the center begins to lose its alignment is just above the MOMBE growth temperature of 500 °C. Our annealing results also show that the 2688-cm^{-1} center studied here is different than the aligned center previously observed by luminescence measurements for GaAs grown by MBE.[34,35,39] The MBE growth temperature was 620 °C, which is greater than the temperature where the 2688-cm^{-1} center loses its alignment.

IV. A MODEL FOR THE 2688-cm^{-1} CENTER AND ITS ANNEALING CHARACTERISTICS

In the following, we suggest that the 2688-cm^{-1} absorption band is due to a pair of C atoms that occupy next-nearest-neighbor As sites (Fig. 5) that bind a single hydrogen atom to account for the concentration of 2688-cm^{-1} centers and their annealing characteristics.

A. Concentration of 2688-cm^{-1} centers: A $(C_{As})_2H$ model

The concentration of a hydrogen-containing complex, N_H, can be estimated from the integrated absorption coefficient A of the center's H-stretching band. The relationship, $N_H = 1.8\times10^{16}$ cm^{-1} A, with A in units of cm^{-2}, was determined previously for the C_{As}-H center.[18,19,29] If we assume that this relationship applies approximately to the 2688-cm^{-1} center as well, then for the sample with $N_A = 2\times10^{20}$ cm^{-3} shown in Fig. 1(a), for example, we find that the concentration of 2688-cm^{-1}

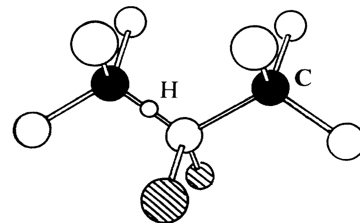


FIG. 5. $(C_{As})_2H$ complex in GaAs with a bond-centered hydrogen atom between a close pair of C_{As} atoms. The C and H atoms are labeled. The atoms drawn as open circles are Ga atoms, and the shaded circles are As atoms.

centers is 2.2×10^{18} cm^{-3}. Similar estimates of the concentration of 2688-cm^{-1} centers for several carbon-doped samples are given in Table I.

With the high concentrations of carbon present in our samples, one expects there to be a substantial concentration of carbon pairs present. If the distribution of C_{As} atoms were random, the concentration N_P of C_{As} pairs formed would be given by

$$N_P/N_{As}=12([C_{As}]/N_{As})^2(1-[C_{As}]/N_{As})^{11} , \quad (2)$$

where N_{As} is the concentration of As sublattice sites. Here the factor of 12 is the number of second-nearest-neighbor sites, the second factor is the probability that two specific next-nearest-neighbor sites will be occupied by C, and the third factor is the probability that the other 11 next-nearest-neighbor sites will contain C. With $[C_{As}]=2\times10^{20}$ cm^{-3} as an example, the number of pairs calculated from Eq. (2) is $N_P=2\times10^{19}$ cm^{-3}. The Coulomb energy associated with pairs of charged acceptors will reduce the number of pairs present. The repulsive Coulomb energy for two charged acceptors at next-nearest-neighbor sites is $E_C=e^2/(4\pi\varepsilon r)=0.27$ eV, where $\varepsilon=13.1\varepsilon_0$ for GaAs, and $r=4$ Å for next-nearest-neighbor sites. This Coulomb repulsion would reduce the number of charged $C_{As}{}^-$ pairs by a Boltzmann factor $\exp(-E_C/kT)=0.02$, at the crystal-growth temperature of 500 °C to $N_P=4\times10^{17}$ cm^{-3} for a sample with $[C_{As}]=2\times10^{20}$ cm^{-3}.

If we neglect the Coulomb repulsion, the estimate of N_P is an order of magnitude larger than the concentration of 2688-cm^{-1} centers we estimate from the strength of the infrared absorption, whereas if we include the Coulomb repulsion our estimate is about a factor of 5 less than the observed concentration. Given the likely errors in the estimates we have made, the agreement of the latter estimate with experiment would be satisfactory and physically reasonable. However, the difference in the behavior of the 2688-cm^{-1} center upon annealing in H_2 or He provides evidence of the involvement of hydrogen in the formation and dissociation of this complex.

The following model for the concentration of 2688-cm^{-1} centers and their annealing behavior is proposed. During growth or annealing in the presence of a source of hydrogen, there will be C_{As}^- acceptors and passivated acceptors, $(C_{As}H)^0$, present. At the high C_{As} concentrations present in our samples, there will be a substantial concentration of $(C_{As}H)^0$-C_{As}^- next-nearest-neighbor pairs present for random distributions of these species. If we assume the fraction of C_{As} acceptors that is complexed with hydrogen at the growth temperature is roughly 10%, as is suggested by previous results on the passivation of heavily carbon-doped GaAs grown by MOMBE (Ref. 29), then the concentration of $(C_{As}H)^0$-C_{As}^- next-nearest-neighbor pairs is estimated to be 1.8×10^{18} cm^{-3} for a sample with $[C_{As}]=2\times10^{20}$ cm^{-3}. [To arrive at this estimate, the result of Eq. (2) is reduced by a factor of 0.09. A factor of 0.1 accounts for the concentration of C_{As}-H centers, and an addition factor of 0.9 accounts for the reduction in the concentration of isolated C_{As} centers when 10% are passivated by hydrogen.] Note that there is no Coulomb repulsion for this pair. Similar estimates are shown in Table I and compared to the concentration of 2688-cm^{-1} centers determined from the strength of the IR absorption for several samples with different acceptor concentrations. The good agreement between these estimates of the concentration of 2688-cm^{-1} centers shows that a $(C_{As})_2H$ center can reasonably account for the concentration of observed 2688-cm^{-1} centers. We note that this model for the concentration of $(C_{As})_2H$ centers assumes that the chemical binding energy between the $(C_{As}H)^0$ and the C_{As}^- components of the complex is negligible.

If we anneal samples containing $(C_{As}H)^0$-C_{As}^- pairs in an ambient that does not contain H at temperatures near 600 °C, hydrogen will dissociate from the center and leave the sample. In this case, the added Coulomb repulsion that results will cause the C_{As}^--C_{As}^- pair to separate if the C_{As} atoms are sufficiently mobile. Our estimates above indicate that the concentration of close pairs would be reduced by a factor of roughly 5 when H leaves the sample. This reduction of the concentration of close pairs is consistent with our observation that if H is reintroduced into a sample at 450 °C, following an anneal in He that causes the 2688-cm^{-1} band to disappear, then no 2688-cm^{-1} centers are formed even though C_{As}-H centers are created.

The model of randomly distributed $(C_{As}H)^0$-C_{As}^- pairs cannot be strictly correct because there would be no preferential orientation. A better model would explain how the 2688-cm^{-1} defects become aligned on the growth surface and treat the formation of complexes along a particular ⟨110⟩ direction on the surface. We do not attempt such a treatment, and only make reference to the previous arguments of Skolnick *et al.*[39] about the inequivalence of the ⟨110⟩ directions on the (001) surface which makes it plausible that aligned complexes can be formed there. In spite of its simplicity, our model roughly accounts for the concentration of 2688-cm^{-1} centers, and provides a mechanism for the dependence of their annealing characteristics upon the ambient.

From our data we cannot determine where the H

TABLE I. The concentration of 2688-cm^{-1} complexes, [2688 cm^{-1}], for several heavily-carbon-doped samples. [2688 cm^{-1}] is estimated from the area of the H-stretching absorption band and a calibration determined previously (Refs. 19 and 29). The concentration of $(C_{As})_2H$ centers is calculated by multiplying the result of Eq. (2) by a factor of 0.09, as is described in the text below Eq. (2). In Eq. (2) we have also taken $[C_{As}]\approx N_A$ for these estimates.

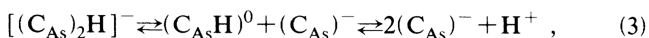
N_A (10^{20} cm^{-3})	x (μm)	[2688 cm^{-1}] (10^{18} cm^{-3})	$[(C_{As})_2H]$ (10^{10} cm^{-3})
0.06	0.73	<0.07	0.002
0.6	1.3	0.77	0.17
0.95	0.33	0.71	0.42
1.5	0.16	1.1	1.0
2.0	0.35	2.2	1.8
4.0	0.25	6.1	6.4

would be located in the $(C_{As})_2H$ complex we have proposed. We suggest that it is in a bond-centered position between one of the C_{As} atoms and the Ga atom that lies between the C atoms of the pair as shown in Fig. 5. In this case, the C atoms would lie along what we have taken to be a $[1\bar{1}0]$ direction to be consistent with the preferential polarization of the absorption at 2688 cm^{-1} along this direction. A bond-centered position with the H atom attached to a C atom would be consistent with the observed vibrational frequency which is close to that of the C_{As}-H complex (which has the H near the bond center between C and a Ga neighbor), and also with the similar isotope shift upon substitution of D for H ($\omega_H/\omega_D \approx 1.339$ for the 2636- and 2688-cm^{-1} bands[19,29]), which further suggests a local bonding configuration that is similar to C_{As}-H. We have suggested the specific bond-centered site shown in Fig. 5 for the hydrogen atom (or the symmetrically equivalent site) because the strain along the $[1\bar{1}0]$ axis associated with the addition of the hydrogen atom can be partially relieved but the carbon atoms which are smaller than the As atoms they replace. The other bond-centered sites surrounding the C atoms shown in Fig. 5, i.e., a site in the (110) plane but not between the C atoms or a site in one of the $(1\bar{1}0)$ planes, would also give rise to polarized absorption bands if the C atoms were aligned, and are also candidates for the location of the H atom in the 2688-cm^{-1} complex.

The two absorption bands at 2643 and 2651 cm^{-1} appear to be due to perturbed C_{As}-H complexes, but remain otherwise unassigned.

B. Loss of alignment and the formation of 2688-cm^{-1} complexes

The loss of alignment of the 2688-cm^{-1} center is explained as follows. When a sample with 2688-cm^{-1} centers that have been aligned during growth is annealed in H_2 at a temperature above $\approx 525\,°C$, then $(C_{As})_2H$ centers will dissociate and reform elsewhere with random orientation, so that an equilibrium in the reactions,



$$[(C_{As})_2H]^- \rightleftarrows (C_{As}H)^0 + (C_{As})^- \rightleftarrows 2(C_{As})^- + H^+ , \quad (3)$$

will be maintained. This mechanism for the loss of alignment for the 2688-cm^{-1} center upon annealing in H_2 requires that if a highly-carbon-doped sample, initially with no 2688-cm^{-1} centers, is annealed in H_2 at temperatures above 525 °C, then $(C_{As})_2H$ complexes will be formed. In Fig. 6(a) is shown the H-stretching spectrum of a sample grown by MOCVD ($N_A = 1.2 \times 10^{20}$ cm^{-3}) in its as-grown state. There is a strong feature at 2636 cm^{-1} due to C_{As}-H, but no 2688-cm^{-1} band. We note that the 2688-cm^{-1} band has not been observed previously by us or by other groups for over a dozen different MOCVD-grown epitaxial layers.[20–22,29] The H-stretching spectrum is shown in Fig. 6 (spectrum *b*) for the same sample following an anneal in H_2 at 600 °C for 30 min in an ampoule that also contained a large amount of GaAs powder to help prevent As loss from the epitaxial layer during the anneal. The band at 2688 cm^{-1} was present after the anneal, and the bands at 2643 and 2651 cm^{-1} were also observed. For this sample, none of these bands was polarized, as is expected.

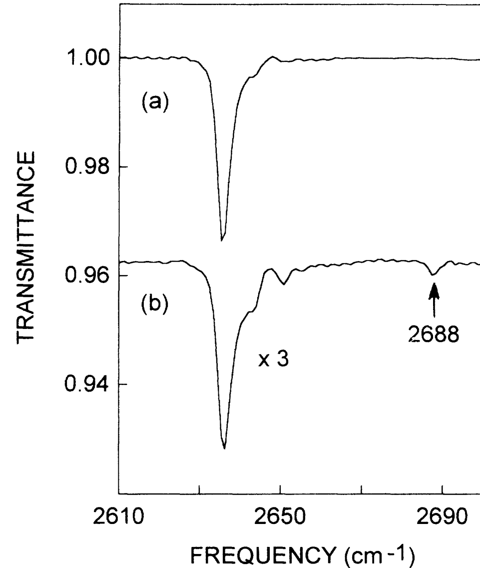


FIG. 6. IR-absorption spectra, measured near 4.2 K with unpolarized light, are shown for heavily carbon-doped GaAs grown by MOCVD with $N_A = 1.2 \times 10^{20}$ cm^{-3}. Spectrum (*a*) shows an as-grown sample. Spectrum (*b*) shows a sample annealed in H_2 at 600 °C for 30 min.

To further explore the temperature dependence of the formation of the 2688-cm^{-1} band, we have annealed several MOMBE-grown samples with $N_A = 5 \times 10^{20}$ cm^{-3} in He at 620 °C for 30 min to eliminate the 2688-cm^{-1} center. Subsequently, we annealed these samples in $\frac{2}{3}$ atm of H_2 for 30 min at several temperatures. The area of the 2688-cm^{-1} absorption band is plotted in Fig. 4 vs the annealing temperature. The 2688-cm^{-1} band begins to reappear for an annealing temperature near 500 °C. In the context of our model, this corresponds to the temperature at which C_{As} becomes sufficiently mobile for $(C_{As})_2H$ complexes to be formed. We note that these results justify assumptions we have made in Sec. IV A above about the mobility of carbon in our samples. The 30-min annealing treatments performed at 450 °C in H_2 to introduce H into heavily-carbon-doped samples are performed at a sufficiently low temperature that carbon is immobile and $(C_{As})_2H$ complexes are not formed. Hence this hydrogen introduction method appears to be benign, and the number of hydrogenated complexes that results should reflect the number of binding sites initially present. Further, when samples are annealed in H_2 or He above 525 °C, the carbon is sufficiently mobile for pair defects to reform elsewhere in a H_2 ambient, or simply to separate in a He ambient.

V. CONCLUSION

In summary, an absorption band at 2688 cm^{-1} observed in heavily-carbon-doped GaAs grown by MOMBE from TMG and AsH_3 has been found to be preferentially polarized along a particular $\langle 110 \rangle$ direction in the (001) growth plane. Our results suggest that H is bound to a

low-symmetry defect, and that this complex has been aligned at the growth surface and has then maintained its alignment as the epilayer was grown. We have studied the annealing of the 2688-cm^{-1} center in H_2 and He ambients, and found that the center is annealed away for temperatures above 525 °C in the He ambient, whereas in a H_2 ambient, it loses it alignment for the same annealing temperatures and is not annealed away until the temperature is increased further. Our results lead us to suggest that the 2688-cm^{-1} center is due to a $(C_{As})_2H$ center, and that the hydrogen in the center controls the pairing and depairing of the C_{As} atoms.

There is insufficient microscopic evidence to prove that the aligned complex to which hydrogen is bound to form the 2688-cm^{-1} center is a C_{As} pair although our results strongly suggest it. The model we have presented accounts roughly for the concentration of centers, and explains the difference in the behavior of the 2688-cm^{-1} center upon annealing in H_2 and He ambients. This model also explains the reorientation of the 2688-cm^{-1} center in a H_2 ambient. Another possible C-pair center that might form in heavily-carbon-doped GaAs is the C_{As}-C_{Ga} pair. This pair does not lead to a model for the annealing behavior of the 2688-cm^{-1} center as readily as the $(C_{As})_2H$ model we have proposed. Further, the stability of the 2688-cm^{-1} band upon annealing has been found to be greater than for the 2636-cm^{-1} band in a previous study.[19,29] This would argue against the 2688-cm^{-1} band being due to a $C_{As}C_{Ga}H$ complex, which would be expected to be less stable than the C_{As}-H-acceptor–hydrogen pair because $C_{As}C_{Ga}$ is a neutral complex and would not be expected to bind hydrogen as strongly as the C_{As} acceptor.

In this work the C-H vibrational modes have provided an excellent probe of carbon-related complexes in heavily-carbon-doped GaAs. The vibrations associated with the carbon atom in the C_{As}-H complex have been studied in detail,[20–22,30,43,44] and there are theoretical predictions for the vibrational modes that should be expected for carbon pairs.[45] An examination of the carbon modes associated with the centers studied here should provide further information about their structures and unusual characteristics.

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