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Symmetry, stress alignment, and reorientation kinetics of the Si_{As}-H complex in GaAs

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The symmetry, reorientation kinetics, and coupling of the ground-state energy to stress have been determined for the Si_{As}-H complex in GaAs from uniaxial stress data. The stress-induced frequency shifts of the H-stretching vibration at 2094.5 cm^{-1} are consistent with trigonal symmetry for the defect. The application of stress at temperatures above 85 K gives rise to a preferential alignment of the defect. The reorientation of the complex is thermally activated with an activation energy of 0.26 eV. The uniaxial stress data are consistent with the hydrogen atom being on the trigonal axis between the Si acceptor and a nearest-neighbor gallium atom.

I. INTRODUCTION

Infrared-absorption spectroscopy has provided an important probe of the microscopic properties of dopant-H complexes in semiconductors. While dopant-H complexes are not usually electrically active or paramagnetic, the localized vibrational modes of the H atom, and sometimes the dopant atom in the complex, are readily studied. The vibrational spectra of several hydrogen-passivated dopants in Si and III-V semiconductors have been assigned.[1-5] An additional perturbationlike uniaxial stress greatly enhances the microscopic properties that can be explored with vibrational spectroscopy. In this paper we present the results of a study of the H-stretching vibration of the Si_{As}-H complex in GaAs under stress to determine the complex's symmetry, reorientation kinetics, and coupling to stress.

The H-stretching vibration at 2094.5 cm^{-1} was assigned to the Si_{As}-H complex by Chevallier *et al.*[6] in a study of *p*-type, Si-doped GaAs grown by liquid-phase epitaxy (LPE) that had been passivated by exposure to a hydrogen plasma. The D-stretching vibration of the Si_{As}-D complex at 1514.5 cm^{-1} was also identified. Chevallier *et al.* suggested that the H atom is near the bond center between the Si_{As} atom and a nearest-neighbor Ga atom by analogy with the well-accepted model for the B-H complex in Si.[7-11] The bond-centered structure for the Si_{As}-H complex is also consistent with that proposed recently in calculations performed for the C_{As}-H complex in GaAs.[12]

The infrared-absorption spectra of a few acceptor-H complexes have been studied under stress. These include the B-H complex in Si,[13-15] the Be_{Ga}-H,[15,16] and C_{As}-H (Refs. 15 and 17) complexes in GaAs, and the Zn_{In}-H complex in InP.[18] All of these centers have been found to have trigonal symmetry and can be aligned by stresses applied below room temperature. In this paper we will find that the Si_{As}-H complex has similar properties under stress.

II. EXPERIMENTAL PROCEDURE

The samples used in our experiments were *p*-type, Si-doped, GaAs epitaxial layers grown by LPE onto 2-mm-thick, semi-insulating GaAs substrates. The thickness of the epilayers was 35 μm. The hole concentration in the epilayers was determined to be 4×10^{18} cm^{-3} from Hall-effect measurements made by the van der Pauw method with HgIn contacts. The as-grown material was cut into bar-shaped samples with approximate dimensions $2\times2\times8$ mm^3 and with the long dimension of the samples oriented parallel to the $\langle 001\rangle$, $\langle 111\rangle$, or $\langle 110\rangle$ crystal directions. The ends of the samples were lapped flat and parallel for the application of stress. To form Si_{As}-H complexes, the samples were exposed to a hydrogen plasma at 250 °C for 90 min in a Technics Planar Etch II plasma reactor.

Stress was applied parallel to the long dimension of the samples by a push-rod stress apparatus. The stress apparatus was fastened to the cold finger of an Air Products Helitran continuous flow cryostat, enabling the sample temperature to be varied between room temperature and $\approx$15 K. This apparatus has been used in several studies and is known to produce a well-calibrated, homogeneous stress. We expect errors due to the miscalibration of the stress to be less than 5%. The temperature of the sample was measured with a Chromel versus Au:(0.07 at. % Fe) thermocouple that was glued to the sample with epoxy. Infrared measurements were made with a Bomem DA3.16 Fourier-transform spectrometer equipped with a KBr beam splitter and an InSb detector. Light was polarized with a wire grid polarizer on a CaF_2 substrate. Spectra were measured near 15 K with a resolution of 2 or 4 cm^{-1}.

III. EXPERIMENTAL RESULTS

A defect in a diamond or zinc-blende lattice may have several crystallographically equivalent orientations, consistent with its symmetry. For example, a defect with tri-

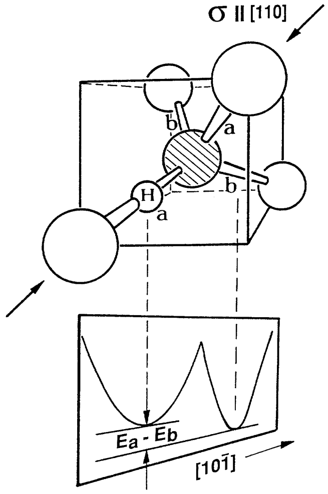

FIG. 1. An acceptor-H complex under [110] stress is shown. n_a and n_b are the populations of the orientations a and b that are made inequivalent by the applied stress. Below, a schematic diagram is shown of the energy of the acceptor-H complex vs position of the H atom in the (101) plane that contains inequivalent orientations. The barrier for reorientation in this plane and the ground-state energy shift (shown exaggerated) are apparent.

gonal symmetry can have its threefold axis along any of the ⟨111⟩ crystal axes. An applied uniaxial stress can lower the symmetry of the crystal and partially lift this orientational degeneracy. For example, the bond-centered configuration of a typical acceptor-H complex (which we will find to be consistent with the data for $\mathrm{Si_{As}}$-H that will be presented below) is shown in Fig. 1 with stress applied along the [110] direction. In this case, the four bond-centered positions for H are divided into two inequivalent pairs labeled a and b.

In Sec. III A results are presented for stresses that were applied at sufficiently low temperature that the $\mathrm{Si_{As}}$-H center cannot reorient among its possible configurations. The applied stress causes the H-stretching band to split into components because the vibrational transition energies of differently oriented complexes are no longer equivalent. The vibrational transition energies of the stress-split components and their intensity ratios were measured with polarized light for three stress directions to determine the symmetry of the center.

The applied stress also gives rise to a shift of the ground-state energy of a defect complex that depends on its orientation (Fig. 1). If the temperature is sufficiently high for the defects to reorient and there has been sufficient time for equilibrium to be established, the populations of the different orientations will be determined by Boltzmann statistics. A preferential alignment of the centers results. For the example shown in Fig. 1, the ratio of the defect concentrations for orientations b and a would be given by

$$n_b/n_a=\exp[(E_a-E_b)/kT] , \tag{1}$$

where E_a and E_b are the ground-state energies of defects with orientations a and b, respectively. The ratio of absorption coefficients for light polarized perpendicular and parallel to the applied stress is used to determine n_b/n_a. If the stress is removed and the temperature is sufficiently high, the centers will redistribute so that the different orientations are equally populated. In Sec. III B we will present data on the kinetics of the redistribution between orientations. In Sec. III C we will present data on the magnitude of the alignment to determine the coupling of ground-state energy to stress.

A. Symmetry of the $\mathrm{Si_{As}}$-H complex

In the following experiments, samples were cooled in the absence of applied stress to 15 K where stress was then applied. It will be shown in Sec. III B that the $\mathrm{Si_{As}}$-H center does not reorient at 15 K. Absorption spectra for the H-stretching band were measured with polarized light for the high-symmetry stress directions. In Fig. 2 it is shown that the H-stretching band is split for the [111] and [110] stress directions but not for [001] stress. Already this suggests that the $\mathrm{Si_{As\text{-}H}}$ defect has trigonal symmetry because the different ⟨111⟩ directions are all at the same angle with respect to a ⟨001⟩ stress axis and remain equivalent.

The energies of the stress-split components of the H-stretching band are plotted as a function of stress for the high-symmetry stress directions in Fig. 3. The components observed for [111] stress with $\mathbf{E}\|\sigma$ were only partially resolved. To determine the position of the stronger, high-frequency component, the spectra were fit with the sum of two Voight-shaped bands. The frequen-

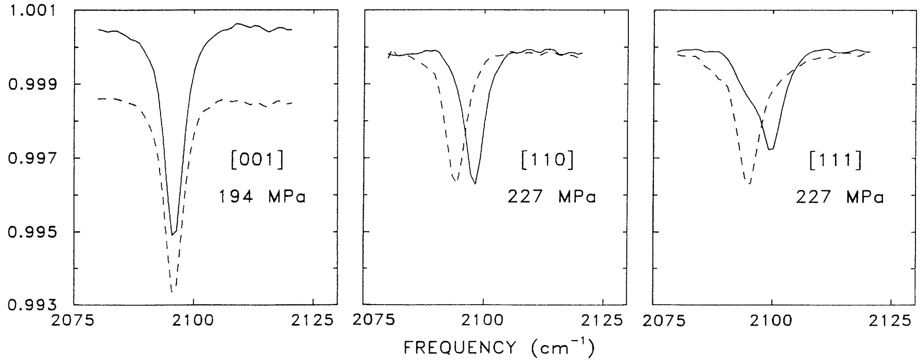

FIG. 2. Effect of stress on the 2094.5-cm^{-1} H-stretching band of the $\mathrm{Si_{As}}$-H complex in GaAs. The stress direction is shown and the polarization of the light is $\mathbf{E}\|\sigma$ (——) and $\mathbf{E}\perp\sigma$ (— — —). Spectra were measured at 15 K. The spectra for [001] stress are displaced vertically for clarity.

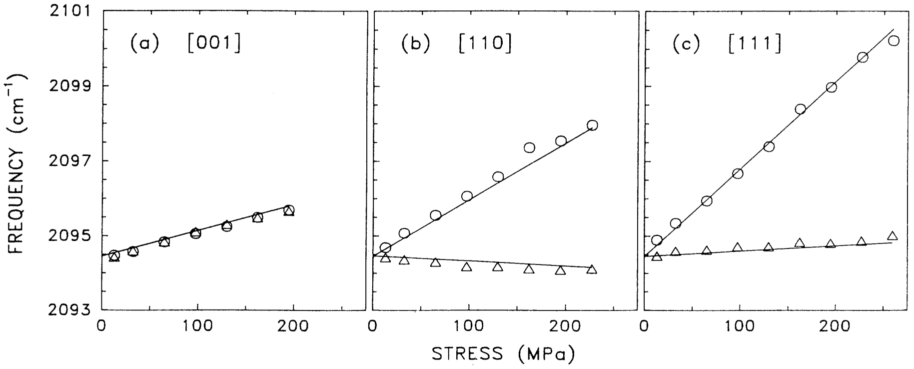

FIG. 3. Stress-induced shifts and polarization characteristics of the 2094.5-cm^{-1} band plotted vs the magnitude of the applied stress. Points for $\mathbf{E}\|\sigma$ are denoted by open circles and points for $\mathbf{E}\perp\sigma$ are denoted by open triangles.

cy of the weaker component was determined from the data measured for $\mathbf{E}\perp\sigma$ and was held fixed to perform the fit. Hence, the position of the shoulder observed for [111] stress with $\mathbf{E}\|\sigma$ was not determined independently and is not plotted in Fig. 3(c).

The splitting pattern and intensity ratios are consistent with those given in Table I for an A_1 mode of a complex with trigonal symmetry.[19] The straight lines shown in Fig. 3 are the result of a least-squares fit of the expressions given in Table I that was made simultaneously to all of the experimental data points. The values of the parameters $A_1=7.0\pm0.4$ cm^{-1}/GPa and $A_2=8.4\pm0.5$ cm^{-1}/GPa, were determined from the fit. Here, and in the following, the sign of a compressive stress is taken to be positive. The errors in these values are determined primarily from an estimate of the uncertainty in the measurement of the sample areas.

B. Reorientation kinetics

The effect of stress applied along a [110] direction at room temperature and then maintained while the sample was cooled to near 15 K is shown in Fig. 4. The absorption for this sample was measured with light propagating along the [001] direction. For this stress and viewing geometry, it can be seen from Table I that only the defects labeled *a* in Fig. 1 contribute to the absorption for $\mathbf{E}\|\sigma$ and only the *b* defects contribute for $\mathbf{E}\perp\sigma$. The relative intensities of the stress-split components have changed from those in the corresponding spectra shown in Fig. 2 because of the redistribution of the $\mathrm{Si_{As}}$-H complexes among the possible ⟨111⟩ orientations that has occurred while the sample was cooled under stress. Here, the absorption for $\mathbf{E}\perp\sigma$ has increased and for $\mathbf{E}\|\sigma$ decreased showing that the sites perpendicular to the stress axis are preferentially occupied.

TABLE I. Stress-induced frequency shift Δ and intensity ratios for the stress-split components of an A_1 mode of a trigonal center. σ is the applied stress. **E** and **k** are the electric vector and propagation direction of the light, respectively (after Kaplyanskii, Ref. 19).

Stress direction	Δ	$\mathbf{E}\|\sigma$	$\mathbf{E}\perp\sigma$
$\sigma\|[001]$	$A_1\sigma$	4	4
$\sigma\|[111]$	$(A_1+2A_2)\sigma$	3	0
	$(A_1-\frac{2}{3}A_2)\sigma$	1	4
$\sigma\|[110]$	$(A_1+A_2)\sigma$	4	0
$\mathbf{k}\|[001]$	$(A_1-A_2)\sigma$	0	4

When the stress is removed after the sample has been cooled under stress to near 15 K, the alignment of the $\mathrm{Si_{As}}$-H centers is frozen in and the optical dichroism, i.e., the anisotropy in the polarized absorption, for the 2094.5 cm^{-1} band remains. The dichroism is defined as

$$D\equiv(\alpha_\perp-\alpha_\|)/(\alpha_\perp+\alpha_\|) . \tag{2}$$

Here, the α's are the absorption coefficients measured perpendicular or parallel to the applied stress direction at the peak of the 2094.5-cm^{-1} band. Upon subsequent annealing in the absence of stress, the complexes will reorient so as to be randomly distributed among the different ⟨111⟩ orientations and the dichroism will disappear.

In these experiments, the sample was initially cooled from room temperature to 15 K under a [110] stress of 225 MPa to align the $\mathrm{Si_{As}}$-H complexes. The stress was then reduced to 12 MPa and the dichroism *D* was measured near 15 K to check the initial alignment. Subsequently, the sample was warmed to the annealing temperature and held at that temperature for 30 min. Finally, the sample was again cooled to 15 K where *D* was remea-

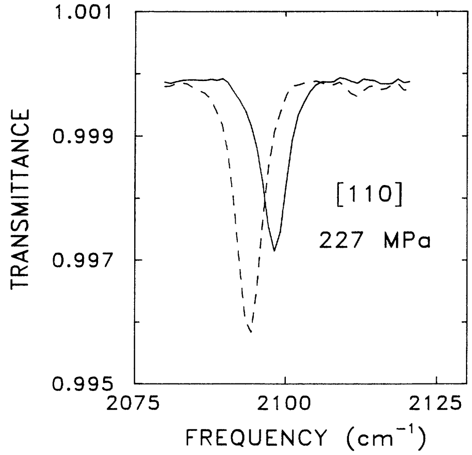

FIG. 4. Transmission spectra of the H-stretching band at 2094.5 cm^{-1} of the $\mathrm{Si_{As}}$-H complex that has been preferentially aligned by an applied stress. A [110] stress of 227 MPa was applied to the sample at room temperature and maintained during the cooldown and subsequent measurement at 15 K. The polarization of the light is $\mathbf{E}\|\sigma$ (——) and $\mathbf{E}\perp\sigma$ (— — —).

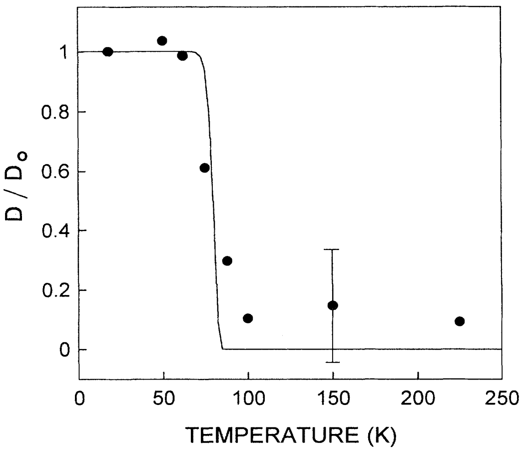

FIG. 5. Isochronal (30 min) annealing data for the decay of the stress-induced dichroism in the H-stretching band of the Si_{As}-H complex in GaAs. The dichroism following the 30-min anneal D is normalized to the dichroism D_0 measured before annealing. The solid line corresponds to an activation energy of 0.26 eV for the reorientation of the complex.

sured. This procedure was repeated for each data point. Typically, the initial value of the dichroism was $D=0.24$. D was measured at 15 K rather than at the annealing temperature because the absorption bands are narrower at low temperature and the peak absorption can be measured more accurately. In Fig. 5 are shown isochronal annealing data for the dichroism.[20]

The stress was reduced to 12 rather than 0 MPa in our experiments because a small stress was required to maintain good thermal contact to the sample in our apparatus so that its temperature could be well controlled. This gives rise to a small residual dichroism in our annealing experiments that can be calculated and accounted for easily from the data presented in the next section. This residual dichroism was calculated to be $D=0.013$ and was subtracted from our measured data.

We assume that the decay of the dichroism follows first-order kinetics and that the rate of decay is thermally activated as was verified previously for the B-H complex in Si.[14] In this case, we have

$$D/D_0=\exp(-k_D t) , \tag{3a}$$

where

$$k_D=\nu_D \exp(-E_A/kT) . \tag{3b}$$

Here, t is the annealing time (1800 s), E_A is the activation energy for reorientation of the complex, T is the annealing temperature, and k_D is the rate of decay of the dichroism. The solid line in Fig. 5 corresponds to an activation energy of $E_A=0.26$ eV. We have assumed an attempt frequency of $\nu_D=1\times10^{13}$ s^{-1}.

C. Ground-state energy shift

When the temperature is sufficiently high for equilibrium between the populations of inequivalent orientations to be established under stress, a measurement of n_b/n_a determines the shift of the ground-state energy from Eq. (1). For a defect with trigonal symmetry, as is the case for the Si_{As}-H complex studied here, stress applied along one direction is sufficient to determine the coupling to stress. In our experiments, a uniaxial stress with magnitude σ_{110} was applied in the [110] direction. For this stress direction and a [001] optical viewing direction, the ratio of the measured absorption coefficients $\alpha_\perp/\alpha_\parallel$ for the H-stretching band gives the population ratio n_b/n_a and from Eq. (1), the ground-state energy shift E_a-E_b.

Based on our results in Sec. III B an alignment temperature of 85 K was chosen for our experiments. The reorientation time constant at 85 K is calculated to be about 4 min. In our experiments, stress was applied for 30 min at 85 K to establish equilibrium. The sample was then cooled quickly with the stress maintained to ≈ 15 K where polarized absorption spectra were measured. The alignment temperature was chosen so that the sample could be cooled sufficiently quickly for the dichroism measured at low temperature to be characteristic of the equilibrium established at the alignment temperature, i.e., the reorientation is sufficiently slow just a few degrees below 85 K that appreciable further alignment did not occur as the sample was cooled. This procedure was repeated for each value of the applied stress. A plot of $\ln(\alpha_\perp/\alpha_\parallel)$ versus σ_{110} is shown in Fig. 6.

The energy of a defect under an applied stress can be written as

$$E=\sum_{ij} A'_{ij}\sigma_{ij} , \tag{4}$$

where the σ_{ij}'s are the components of the stress tensor and the A'_{ij}'s are the components of the piezospectroscopic tensor.[19] The prime has been added to the components of the piezospectroscopic tensor to distinguish the parameters that characterize the ground-state energy shift from those that characterize the transition-energy shifts discussed in Sec. III A. For a defect with trigonal symmetry, Kaplyanskii[19] has shown that $\mathbf{A}'$ has only two independent components, A'_1 and A'_2. In the principal axis coordinate system of the trigonal defect with the x_3

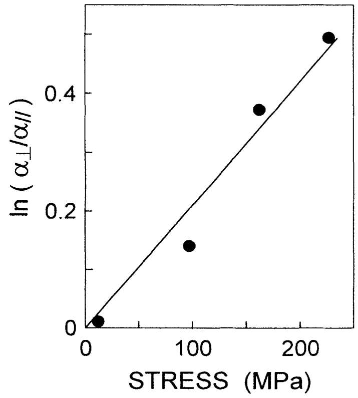

FIG. 6. ln $(\alpha_\perp/\alpha_\parallel)$ vs the magnitude of stress applied along the [110] direction at 85 K. The line shown has a slope of 2.1 GPa^{-1}.

TABLE II. Parameters that characterize the properties of a few trigonal acceptor-H complexes in Si and GaAs under stress. The sign of compressive stress is defined to be positive.

	A_1 (cm^{-1}/GPa)	A_2 (cm^{-1}/GPa)	A'_2 (meV/GPA)	E_A (eV)	References
Si:B-H	12.7	13.5	11.6	0.22	13,14,15
GaAs:Be$_{Ga}$-H	5.0	6.5	9.3	0.37	15,16
GaAs:Si$_{As}$-H	7.0	8.4	7.8	0.26	
GaAs:C$_{As}$-H	2.4	2.5	8.2	0.50	15,17

axis along the threefold axis, the nonzero components of the piezospectroscopic tensor are

$$A'_{11}=A'_{22}=A'_1-A'_2 \tag{5a}$$

and

$$A'_{33}=A'_1+2A'_2\ . \tag{5b}$$

In an experiment like ours, the alignment depends only on the difference in energy between different orientations, hence the coupling A'_1 to the hydrostatic component of the stress cannot be determined. For a stress along the [110] axis, Eqs. (4) and (5) lead to

$$A'_2=(E_a-E_b)/2\sigma_{110}\ . \tag{6}$$

From Eqs. (1) and (6) one finds that the slope of a plot of $\ln(n_a/n_b)$ versus σ_{110} is $2A'_2/kT$ where T is the alignment temperature. From the data in Fig. 6, the value, $A'_2=7.8\pm1$ meV/GPa, was obtained.

IV. CONCLUSION

The values of the parameters determined in this paper for the properties of the Si$_{As}$-H complex under stress are compared in Table II to those measured previously for acceptor-H complexes in GaAs and the B-H complex in Si. The properties of all of these acceptor-H complexes are similar. The three centers studied all have trigonal symmetry, activation energies for reorientation of a few tenths of an eV, and stress coupling parameters for both the vibrational transition energies and ground-state energies that are similar in magnitude. The B-H complex has been studied most extensively by both theory and experiment and, hence, its structure is the best established.[7–11] The similarity of the vibrational spectra and the characteristics of the Si$_{As}$-H complex under stress to the B-H complex provide the strongest evidence that the hydrogen atom in the Si$_{As}$-H center also has a bond-centered configuration as was suggested originally by Chevallier *et al.*[6] Calculations[12,21] show that the H atom is near the bond center between the acceptor atom and one of its nearest neighbors for the Be$_{Ga}$-H and C$_{As}$-H complexes as well.

Of the acceptor-H centers, only the energy surface for the B-H complex has been studied in detail.[8,22,23] Calculations find that there is a low-energy shell on which H can move about the B atom with an activation energy of 0.2 eV. The data shown in Table II suggest that the situation is similar for all of the acceptor-H complexes in GaAs that have been examined. In several studies,[4,5,24] it has been suggested that for Ga-site acceptors, H is bonded primarily to one of the acceptor's As nearest neighbors. For the As-site acceptors, it has been suggested that hydrogen is bonded primarily to the acceptor atom. Hence, it is surprising that the properties under stress of the acceptor-H complexes for acceptor atoms on the different sublattices in GaAs are so similar, given the suggested differences in local bonding. A comparison of the theoretical total-energy surfaces and the pathways for reorientational motion for hydrogen complexed with acceptors on the Ga and As sublattices would be welcome.

Note added in proof: We have recently become aware of a paper [L. Pavesi and P. Giannozzi, Phys. Rev. B **43**, 2446 (1991)] in which the configuration with the hydrogen near the bond center between the Si$_{As}$ acceptor and a Ga nearest neighbor was found by first-principles calculations to minimize the total energy for the Si$_{As}$-H complex in GaAs.

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