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Structure and dynamics of the Be-H complex in GaAs

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The symmetry and reorientation kinetics of the Be-H complex in GaAs have been determined in a uniaxial-stress study. The splitting of the 2036-cm^{-1} vibrational absorption band under stress shows that the complex has trigonal symmetry. The size of the splitting is large and is consistent with a bond-centered position for the H atom, similar to the case of B-H in Si. At temperatures near 120 K the complex can be aligned by an applied stress. A study of the annealing kinetics of the alignment shows that the motion of H from bond-centered site to bond-centered site about the Be acceptor is thermally activated with an energy of 0.37 eV.

The passivation of shallow impurities in semiconductors by atomic hydrogen gives rise to complexes that include the shallow donor or acceptor and hydrogen.[1-3] The static structures of such complexes have been studied by several techniques, especially for the Si host.[4-13] In addition, the dynamics of H-containing complexes are of interest because of the ease with which the light H atom can move in favorable cases.[3,14-17] In comparison to Si, relatively little is known about shallow-impurity passivation in III-V materials, although this situation is changing rapidly.[18] There have been several infrared absorption studies of both donor-H (Ref. 19) and acceptor-H (Refs. 20 and 21) complexes in GaAs and theoretical calculations[22] are helping to unravel the structures of the defects. Here, we describe a uniaxial-stress study of the vibrational absorption band at 2036 cm^{-1} due to the Be-H complex[21] in GaAs. Both the kinetics of reorientation and symmetry of the complex have been determined.

The acceptor-H complexes in GaAs, for the Ga-site acceptors Zn and Be, are believed to have a bond-centered (BC) configuration with the H between the acceptor and one of its As neighbors, similar to the B-H complex in Si.[18,20-22] Further, the vibrational absorption of the GaAs:Be-H complex[21] is very similar to that of Si:B-H (Ref. 23). [The H stretching vibration is near 2000 cm^{-1}, the line is broad (a few cm^{-1}), and no wagging mode is observed, presumably because it is at low frequency and may lie in the region of strong intrinsic GaAs absorption.] It has been recently discovered by a stress-induced dichroism technique that the B-H complex in Si can reorient among the four equivalent BC configurations.[16] The reorientation of the complex is thermally activated with an energy of 0.19 eV in agreement with the calculation by Denteneer *et al.*[12] The similarities between Si:B-H and GaAs:Be-H have motivated this study of the reorientation kinetics of the Be-H complex. Further, while recent studies of acceptor-H complexes in GaAs (Refs. 18, 20, and 21) are interpreted in terms of a trigonal, BC structure, in agreement with theoretical expectations,[22] we are aware of no direct experimental evidence for trigonal symmetry.

The samples for our experiments were prepared from semi-insulating, Bridgman-grown, GaAs that was ion implanted with Be at energies of 40, 120, 200, and 400 keV each to a dose of 4×10^{14} cm^{-2}. The implants were activated by a rapid thermal anneal at 850 °C for 3 s. Oriented bar-shaped samples with dimensions $2\times2\times8$ mm^3 were prepared for stress studies. These samples were then hydrogenated in a Technics Planar Etch II plasma reactor at 200 °C for 2 h. The infrared absorption was measured with a Nicolet 60SX Fourier-transform spectrometer equipped with an InSb detector. The resolution was 2 cm^{-1}. The incident light was polarized with a wire-grid polarizer on a KRS-5 substrate. Our apparatus for applying uniaxial stress at low temperatures has been used in many studies and is known to produce a homogeneous, well-calibrated, uniaxial stress. The temperature of the sample was measured by a Chromel versus Au:(0.07 at.% Fe) thermocouple that was bonded to the sample with silver epoxy.

Two different types of stress experiment will be described below.[24] In the first set of experiments, stress is applied to the sample at low temperature where the Be-H center is static and cannot reorient among its possible configurations on the time scale of the measurement. The applies stress lowers the symmetry of the crystal and causes centers along directions that have been made inequivalent by the stress to have different vibrational frequencies. The symmetry of the center is determined from the number of stress-split components and their intensity ratios for several orientations of the stress. In the second set of experiments, stress is applied at temperatures sufficiently high for the center to reorient. The applied stress splits the ground-state energy of the differently oriented centers; the different orientations are then populated according to their Boltzmann factors. The absorption of polarized light is sensitive to the orientations of the centers because the H stretching vibration has its transition moment oriented along the Be-H axis. Hence, the difference in absorption for light polarized parallel and perpendicular to the applied stress can be related to the preferential occupation of the low-energy sites. When the stress is removed the centers will redistribute so that the different orientations are equally populated. A study of the kinetics of the redistribution when the stress is removed gives an activation energy for the reorientation of the center.

The effect of stress upon the 2036-cm^{-1} longitudinal H stretching band of the Be-H complex is shown in Fig. 1(a). The stress was applied near 15 K where the complex is static. The splitting pattern and intensity ratios are consistent with trigonal symmetry for the complex (see Table I). In Fig. 2 the line positions as a function of stress are plotted for the high-symmetry stress directions. The straight lines are given by the expressions in Table I with parameters $A_1=0.50\times10^{-2}$ cm^{-1}/MPa and $A_2=0.65\times10^{-2}$ cm^{-1}/Mpa. The stress-split components for the [111] stress direction are partially resolved for **E**∥**F** only for the largest stresses used. (**E** is the electric vector of the incident light and **F** is the applied stress.) We have not tried to determine the position of the lower intensity component for any but the largest [111] stresses because the parameters A_1 and A_2 are well determined by the [001] and [110] results and the trigonal symmetry of the complex is clear.

In Fig. 1(b) we show the effect of stress that had been applied at room temperature and maintained while the sample was cooled to near 15 K. The relative intensities of the stress split components have changed from those shown in Fig. 1(a). The stress-induced dichroism (i.e., the difference in absorption for the bands with **E**∥**F** and **E**⊥**F**) for the [110] stress direction, for example, is due to the stress-induced redistribution of the Be-H complexes among the BC configurations that has occurred while the sample was cooled under stress. Here, the absorption for **E**⊥**F** increases and for **E**∥**F** decreases showing that the sites perpendicular to the stress axis are preferentially occupied. The orientation dependence of the stress-induced anisotropy is also consistent with trigonal symmetry. There is no effect for [001] stress because the ⟨111⟩ axes of the four BC sites are all at the same angle to the [001] stress axis. Both [110] and [111] stress directions lift the orientational degeneracy of the four BC sites and give rise to an optical dichroism. When the stress is removed near 15 K the alignment of the Be-H centers is frozen in and the optical dichroism for the 2036-cm^{-1} band remains.

TABLE I. Stress-induced frequency shift, Δ, and intensity ratios for the stress-split components of an A_1 mode of trigonal center. **F** is the applied stress, σ the magnitude of the stress, **E** the electric vector, and **k** the propagation vector of the light. (Taken from Ref. 25.)

Stress direction	Δ	**E**∥**F**	**E**⊥**F**
F∥[001]	$A_1\sigma$	4	4
F∥[111]	$(A_1+2A_2)\sigma$	3	0
	$(A_1-2/3A_2)\sigma$	1	4
F∥[110]	$(A_1+A_2)\sigma$	4	0
k∥[001]	$(A_1-A_2)\sigma$	0	4

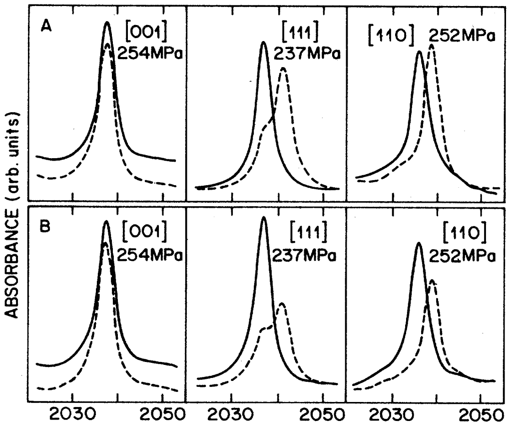

FIG. 1. Effect of stress on the 2036-cm^{-1} H-stretching band of the Be-H complex. **E**∥**F** (---) and **E**⊥**F** (——). The traces for [001] stress are displaced vertically. For (a) the sample was cooled to near 15 K without stress. Stress was subsequently applied near 15 K. For (b) the sample was cooled from room temperature to 15 K with the stress applied. The peak absorbance of the 2036-cm^{-1} band was typically 4×10^{-3} and the linewidth was 4.3 cm^{-1} for our samples.

Upon subsequent annealing in the absence of stress, the stress-aligned Be-H complexes will reorient so as to be randomly distributed among the different ⟨111⟩ orientations and the optical dichroism will disappear. The reorientation of the complex involves an H jump from one BC site to another as is shown in Fig. 3. The Be atom also moves when the hydrogen atom moves because of the relaxation that occurs when the H interrupts the Be—As bond.[22] We expect and have drawn schematically a pathway for H motion similar to that determined theoretically[12] for Si:B-H although there is no direct evidence for this pathway at present.

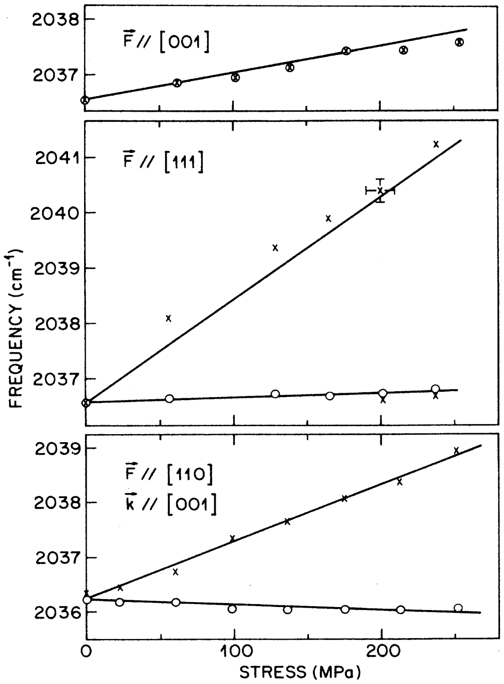

FIG. 2. Stress-induced shifts and polarization characteristics of the 2036-cm^{-1} band. Points for **E**∥**F** are denoted by ×, and points for **E**⊥**F** are denoted by o.

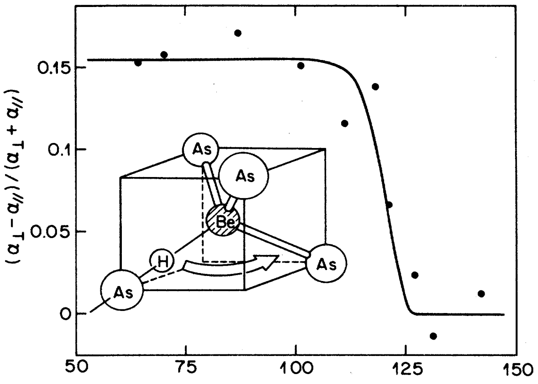

FIG. 3. Decay of stress-induced dichroism as a function of isochronal (20 min) annealing temperatures. The solid line corresponds to an activation energy of E_A of 0.374 eV for reorientation of the complex. The inset shows the GaAs:Be-H complex and the hydrogen jump from BC site to BC site by which the complex reorients.

In Fig. 3 is shown isochronal annealing data for the dichroic ratio, $D \equiv (\alpha_\perp - \alpha_\parallel)/(\alpha_\perp + \alpha_\parallel)$. Here, the α's are the absorption coefficients measured perpendicular or parallel to the applied stress direction at the peak of the 2036 cm^{-1} band. In these experiments, the sample was initially cooled from 180 to 15 K under a [110] stress of 250 MPa to align the Be-H complexes. The dichroic ratio D was measured without stress near 15 K to check the initial alignment. Subsequently, the sample was warmed to the annealing temperature and held at that temperature for 20 min. Finally, the sample was again cooled to 15 K where D was remeasured. This procedure was repeated for each data point. Typically, the initial value of the dichroic ratio was $D = 0.15$. D was measured at low temperature rather than at the annealing temperature to minimize the width of the absorption band, thereby facilitating the determination of the band's baseline and more accurate values of D.

The data in Fig. 3 are fit by the expression

$$D = D_0 \exp(-4k_R t) , \tag{1a}$$

where

$$k_R = \nu_0 \exp(-E_A/kT) . \tag{1b}$$

Here t is the annealing time (1200 s), E_A is the activation energy for reorientation of the complex, and k_R is the rate of reorientation. The rate of decay of dichroism k_D is related to the reorientation rate of the complex by $k_D = 4k_R$ as is expressed in Eq. (1a).[16] The solid line in Fig. 3 corresponds to an activation energy of $E_A = 0.374$ eV. We have assumed an attempt frequency of $\nu_0 = 10^{12}\ \mathrm{s}^{-1}$ based upon our experience[16] with Si:B-H. E_A is insensitive to the value of ν_0 and changes by only 0.02 eV for an order of magnitude change in ν_0.

In summary we have shown that the GaAs:Be-H complex is static at low temperature and that the symmetry of the center is trigonal. There is an anomalously large dependence of the H stretching frequency upon stress (approximately 10 times what is expected for local vibrational modes.) At temperatures near 120 K and above the complex can reorient among its BC configurations by thermally activated jumps of the H atom. The activation energy is 0.37 eV. All of these properties are very similar to those of Si:B-H that have been determined previously.[7,16] Our results provide strong support for similar structures for GaAs:Be-H and Si:B-H and also similar pathways for H motion in these complexes.

The new results for GaAs:Be-H show that the thermally activated motion of H from BC site to BC site, initially observed for Si:B-H, is a common property of such complexes. It is likely that such motions will be found for other acceptor-H complexes as well. The H motion is explained well for Si:B-H by theoretical work[12,13] that shows that the H can move off the [111] axis without raising the energy of the complex significantly. Other properties of the acceptor-H complexes, such as the broad low-temperature linewidth, the lack of an H transverse mode in the 600–800 cm^{-1} region, and the strong coupling to the stress are also likely to be related to the softness to off-axis motions and distortions but are not understood at present.

We also contrast our results to the properties of the Si:Be-H and Ge:Be-H complexes.[14,26] Be is a double acceptor in Si and Ge and can bind an H atom to give a single acceptor complex. In Si the H tunnels about the Be atom. The tunneling splittings add structure to the effective-mass levels and also have been observed directly in far infrared absorption experiments.[14] In Ge, Be-H is a static, trigonally distorted complex[26] and thermally activated reorientation has not been reported. GaAs:Be-H appears to be distinct from the Be-H complexes in Si and Ge; the observation of thermally activated motion rules out low-temperature tunneling for the H. The reason for the difference between the behaviors of these complexes is not clear at present, partly because the structures of Si:Be-H and Ge:Be-H are not known.

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