Evidence of a sulfur-boron-hydrogen complex in GaAs grown by the liquid encapsulation Czochralski technique

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In LEC-grown GaAs:S, two vibrational absorption lines are measured at 2382.2 and 2392.8 cm\(^{-1}\) \((T=7\ \text{K})\) and assigned to \(^{11}\text{B}\)-H and \(^{10}\text{B}\)-H stretching modes. Uniaxial stress experiments reveal that the symmetry of the responsible complex is \(C_\text{s}\). Bond strength considerations suggest that this complex is a \(\text{S}_{\text{As}}\cdot\text{B}_{\text{Ga}}\) pair passivated by hydrogen bonded to boron. The constituents of this S-B-H complex are located within a \{110\} plane.

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I. INTRODUCTION

GaAs single crystals for substrates up to diameters of 6 inches are grown by the liquid encapsulation Czochralski (LEC) technique. This growth technique implies the unavoidable presence of the light-element impurities carbon, nitrogen, boron, oxygen, and hydrogen in the grown GaAs. The water-containing boric oxide \((\text{B}_2\text{O}_3)\) encapsulant is at the origin of boron, oxygen, and hydrogen contamination; moreover the use of pyrolytic boron nitride crucibles can also be at the origin of boron contamination. Hydrogen can be bonded to these light impurities giving rise to local vibrational modes with frequencies far above the intrinsic lattice absorption. These vibrational modes can be measured by Fourier transform infrared (FTIR) absorption spectroscopy and their analyses give information about the hydrogen-impurity complexes. Several complexes of hydrogen with oxygen, carbon, and nitrogen have already been investigated and some knowledge about their structure is available.\(^1\)–\(^6\) However, up to now there is no evidence for a boron-hydrogen complex neither in GaAs nor in other III-V compounds. It has to be noted that substitutional boron \((\text{B}_{\text{Ga}})\) is an isoelectronic impurity, i.e., it is neutral in the GaAs lattice and should not attract charged hydrogen. On the other hand, the complex of hydrogen with the isoelectronic substitutional nitrogen \((\text{N}_{\text{As}})\) exists and is well investigated;\(^3\) this is due to the large nitrogen electronegativity. In \(n\)-type GaAs doped with group-VI donors, it has been shown that hydrogen makes complexes with the donors in which it is located in an antibonding position close to one of the gallium atoms nearest neighbors to the chalcogen.\(^7\)–\(^9\) In this paper, it is shown that in LEC-grown GaAs doped with sulfur, the sulfur atom tends to sit close to a boron atom and hydrogen binds boron.

II. EXPERIMENTAL DETAILS

The GaAs samples investigated are taken from different parts of two boules grown by the liquid encapsulation Czochralski (LEC) technique and doped with sulfur. They are slightly \(n\) conducting \((n=0.5\ \text{to } 2\times10^{17}\ \text{cm}^{-3})\) because of sulfur doping. The boron content in the samples is about \(2\times10^{17}\ \text{cm}^{-3}\) derived from the intensity of the \(^{11}\text{B}_{\text{Ga}}\) local vibrational mode absorption at 517.3 cm\(^{-1}\). The infrared absorption experiments have been performed with either a Bruker IFS 120 HR or a Bomem DA3+ Fourier transform spectrometer using spectral resolutions from 0.05 to 0.2 cm\(^{-1}\). The samples were investigated in the temperature range from 7 to 300 K mounted in Oxford Instruments optical cryostats. Experiments with applied uniaxial stress were carried out using a home made push rod apparatus inserted inside one of the cryostats. The oriented samples for the stress experiments have the dimensions \(10\times4 \times 2.5\ \text{mm}^3\) with the long edges along to the three main crystallographic directions.

FIG. 1. Absorption spectrum of a GaAs:S sample measured at \(T=7\ \text{K}\) with a resolution of 0.08 cm\(^{-1}\) showing the \(^{11}\text{B}_{\text{Ga}}\)-H stretching modes. The inset shows the absorption line assigned to the \(^{11}\text{B}_{\text{Ga}}\)-H wagging mode. The background due to the absorption of the conduction electrons has been subtracted in both spectra.
molecules are around 2600 cm\(^{-1}\). Therefore, the downshift of corresponding molecules. The frequencies of the B–H bonds in bonds in GaAs are about 10 to 20\% smaller than in corre-

dos of hydrogen directly bonded to the isotopes \(^{11}\)B Ga and \(^{10}\)B Ga of substitutional boron in GaAs. The main arguments

to that of the \(^{11}\)B Ga–H stretching mode \(\Gamma\) with \(\Gamma/\Gamma'\approx 1\). A cor-

temperature dependence of the shift and the broadening of lines are still measurable at \(T = 300\) K and Fig. 2 shows the temperature dependence of the shift and the broadening of both lines confirming their vibrational nature.

The two vibrational lines can be assigned to the stretching modes of hydrogen directly bonded to the isotopes \(^{11}\)B Ga and \(^{10}\)B Ga of substitutional boron in GaAs. The main arguments in favor of this interpretation are the following:

(i) The ratio of their integrated intensities of about 4 fits very well that of the natural abundances of \(^{11}\)B/\(^{10}\)B = 4.

(ii) The difference \(\Delta \omega = 9.6\) cm\(^{-1}\) of the vibrational frequencies for the two isotopes is very close to that calculated for a "free" diatomic B–H molecule having a frequency of 2392.8 cm\(^{-1}\) for the \(^{10}\)B–H bond (\(\Delta \omega_{\text{calc}} = 9.9\) cm\(^{-1}\)).

(iii) The frequencies of the C\(_{\text{As}}\)-H, N\(_{\text{As}}\)-H, and Si\(_{\text{Ga}}\)-H bonds in GaAs are about 10 to 20\% smaller than in corresponding molecules. The frequencies of the B–H bonds in molecules are around 2600 cm\(^{-1}\). Therefore, the downshift of about 200 cm\(^{-1}\) found for B\(_{\text{Ga}}\)-H in GaAs is consistent with this rule.\(^{10}\)

In the spectral region where a wagging mode connected with the B–H stretching modes can be expected, indeed a vibrational line at 897.6 cm\(^{-1}\) (\(\Gamma = 0.09\) cm\(^{-1}\)) is observed (see inset of Fig. 1). Its integrated intensity \(I^w\) is correlated to that of the \(^{11}\)B Ga–H stretching mode \(I'\) with \(I'/I^w\approx 1\). A cor-

An estimation of the concentration of the detected B–H center gives [B–H] = 2 x 10\(^{-14}\) cm\(^{-3}\), using the calibration factor of the C–H stretching mode.\(^{11}\) This means that about 0.1\% of the B\(_{\text{Ga}}\) present in the samples is complexed with hydrogen.

IV. EXPERIMENTS WITH UNIAXIAL STRESS

To get more information about the structure of the B–H complex, experiments under uniaxial stress have been performed on the \(^{11}\)B–H line at 2383.2 cm\(^{-1}\) with stresses \(\sigma\) up to 240 MPa applied along the (001), (111), and (110) crystallographic directions and polarized light with its electric vector \(E\) parallel or perpendicular to the stress directions; for \(\sigma\parallel(110)\), the perpendicular polarization corresponds to \(E\parallel[1\overline{1}1]\). This line splits into two components for stress \(\sigma\parallel(001)\), with the relative intensities of both components depending on the polarization of the light. This splitting clearly indicates that the B–H complex does not have trigonal symmetry. For stress \(\sigma\parallel(111)\) a splitting into three components is observed with strongly differing intensity ratios for the two polarization directions. The splitting behaviors for \(\sigma\parallel(001)\) and \(\sigma\parallel(111)\) correspond to those given in Table I and show that the symmetry type of the B–H complex is monoclinic I.\(^{12}\) For centers of this symmetry, as shown in Table I, a splitting into four components should occur for \(\sigma\parallel(110)\); only three components were observed as shown in Fig. 3. From the shifts and splittings for \(\sigma\parallel(001)\) and \(\sigma\parallel(111)\) the fitting parameters defined in Table I for a monoclinic I type center (symmetry \(C_2\)) in a cubic crystal can be derived: \(A_1 = +5.3\) cm\(^{-1}\)/GPa, \(A_2 = -1.1\) cm\(^{-1}\)/GPa, \(A_3 = +2.2\) cm\(^{-1}\)/GPa, and \(A_4 = +1.1\) cm\(^{-1}\)/GPa, a compressive stress being considered as positive. As can be seen in Fig. 3, this set of parameters describes well also the splitting pattern for stress \(\sigma\parallel(110)\); in particular, the frequency difference of two of the four components is very small up to the highest stress values used, so that only three components are measurable.

V. DISCUSSION

Two most important points have to be noted. (i) Even though sulfur and hydrogen are present in the LEC-grown samples used in this study, no “traditional” trigonal sulfur-hydrogen complexes are observed in the material. (ii) A large variety of semi-insulating GaAs samples was investigated with boron contents \(2 \times 10^{16}\) cm\(^{-3}\) < [B\(_{\text{Ga}}\)] < \(2 \times 10^{18}\) cm\(^{-3}\) and resistivities in the range \(10^2 - 10^6\) \(\Omega\) cm, in which no trace of the B–H lines could be detected, even
The Fermi level is within the conduction band at or above $E_F$ located at or below $E_c$. Hydrogen migrates in GaAs as $H^+$ when the Fermi level is in the negative charge state; therefore $H^+$ is responsible for the formation of the detected B-H complexes.

Isolated substitutional boron on Ga site is an isoelectronic impurity, i.e., $B_{Ga}$ is neutral in the GaAs lattice. Therefore, a complexing of $H^-$ with this impurity is hardly understandable. This suggests that a positively charged complex consisting of $B_{Ga}$ and an additional defect must attract $H^-$. The favorite for this defect is the sulfur donor, present in the samples as dopant with a concentration about $10^{17}$ cm$^{-3}$. As a matter of fact, boron sulfur bonds are very strong (581 kJ mol$^{-1}$ in gaseous phase) and are therefore favored in order to minimize the total energy of the crystal; this is why the number of pairs formed is clearly larger than the one expected from a purely statistic distribution of sulfur and boron atoms. In $n$-GaAs the S donor is positively charged, therefore the $S_{As}$-$B_{Ga}$ pairs are positively charged. Thus $H^-$ can be attracted by $S_{As}$-$B_{Ga}$ and passivate the sulfur donor by forming a bond with the neighboring $B_{Ga}$. This is, basically, the same process as verified for the passivation of the group-VI donors S, Se, and Te in GaAs, where the passivating $H$ is bonded to one of the four Ga nearest neighbors to the chalcogen donor in an antibonding position. One can explain that the $H$ passivating the $S_{As}$-$B_{Ga}$ pair is bonded to boron and not to one of the three surrounding Ga as follows. To minimize the total energy of a hydrogen related complex in a solid, hydrogen tends to bind to that atom, with which it has the strongest bond. The bond strength (in gaseous molecules) of B-H is 340 kJ mol$^{-1}$, i.e., considerably larger than for Ga-H (274 kJ mol$^{-1}$). It must also be noted that in LEC-grown materials, only hydrogen complexes that are stable up to rather high temperatures are present, this is not the case for complexes involving Ga-H bonds.

As proposed theoretically and confirmed by uniaxial stress experiments on the vibrational lines of “traditional” passivated chalcogen donors ($D_{As}$), hydrogen is bonded to a Ga nearest neighbor in an antibonding position and directed along (111), i.e., the $D_{As}$-Ga-H complex in GaAs has trigo-
the symmetry elements are the \{110\} mirror planes. For such a center, it has been shown\textsuperscript{15,16} that the intensities of the split components for the two polarizations depend upon the angle \( \Theta \) in the \{110\} plane between the dipole moment of the vibrational mode and the \langle 001 \rangle axis (see Fig. 4); these dependencies are given in Table I. The intensity ratios of the split components for \( \sigma||\langle 001 \rangle \) and \( \sigma\parallel\langle 111 \rangle \) measured with parallel and perpendicular polarization could be fairly well fitted with an angle \( \Theta = 70^\circ \pm 5^\circ \).

Because of the low signal to noise ratio for the split components, the estimated angle \( \Theta \) is not very accurate, compared with the \( \Theta \) values derived for the passivated S, Se, and Te donors in GaP, where the \( \text{D}_{\text{p-P-H}} \) complexes have also the symmetry \( C_{\text{s}} \).\textsuperscript{17} Therefore, the experimental results allow to propose the microscopic model for the \( \text{S}_{\text{As-B Ga-H}} \) complex schematized in Fig. 4. The three constituents are located within a \{110\} plane and there are twelve equivalent configurations of the complex. The antibondinglike position of the hydrogen also explains the occurrence of a wagging mode at frequencies as high as about 900 cm\(^{-1}\).

\begin{align*}
\Delta \omega = \frac{\delta \omega}{e^{\hbar \omega_0/kT} - 1} \\
\Gamma = \frac{2(\delta \omega)^2}{\eta} \left( \frac{1}{2} + \frac{1}{e^{\hbar \omega_0/kT} - 1} \right)^2,
\end{align*}

where \( \delta \omega \) and \( \eta \) are the parameters defined by Persson and Ryberg.\textsuperscript{18} The temperature dependences of the complex involving \( ^{11}\text{B} \) can be fitted with \( \omega_0 = 115 \text{ cm}^{-1} \), \( \delta \omega = -2.44 \text{ cm}^{-1} \), \( \eta = 10.6 \text{ cm}^{-1} \) and the one involving \( ^{10}\text{B} \) with \( \omega_0 = 120 \text{ cm}^{-1} \), \( \delta \omega = -2.67 \text{ cm}^{-1} \), \( \eta = 10.6 \text{ cm}^{-1} \). The lines in Fig. 2 represent the fit of the experimental data with these parameters. \( \omega_0 \) is about 4\% larger for the \( ^{10}\text{B} \) mode than for the \( ^{11}\text{B} \) mode. This isotopic effect indicates that the low-frequency mode, to which the high-frequency B-H stretching mode is coupled, is not a lattice phonon mode, but a low-frequency mode of the S-B-H complex in resonance with the lattice modes. It has to be noted that the \( \omega_0 \) values found above are very close to the frequency of the boron related resonant mode observed in LEC-grown GaAs.\textsuperscript{19}

VI. CONCLUSION

In this paper, it has been shown that in sulfur doped LEC-grown GaAs, the complexes resulting from the neutralization of the sulfur donors by hydrogen involve boron atoms unintentionally present in the material. In these complexes, boron is a nearest neighbor of sulfur and hydrogen is bonded to boron. The reason for the occurrence of this complex only is that the total energy of the crystal with it is lower than with the “traditional” trigonal complex and is, therefore, stable to higher temperatures.

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