

## Raman spectroscopy of hydrogen molecules in GaAs

A. W. R. Leitch\* and J. Weber

Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-70506 Stuttgart, Germany

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The room temperature Raman vibrational modes of isolated  $H_2$ ,  $D_2$ , and HD molecules in GaAs exposed to a  $H_2$ ,  $D_2$ , and  $H_2:D_2$  plasma, have been measured at 3911, 2827, and 3429  $cm^{-1}$ , respectively. At low temperatures the ortho-para modes of the  $H_2$  line are resolved. Decreasing the temperature to 10 K causes the  $H_2$  Raman frequency to increase by 14 to 3925  $cm^{-1}$ . A lack of splitting of the  $H_2$  mode under uniaxial stress confirms that the  $H_2$  molecule is free to rotate within the GaAs lattice. [S0163-1829(99)09043-8]

Hydrogen is a technologically important impurity in GaAs which may have a dramatic influence on the electrical and optical properties of a fabricated device.<sup>1</sup> Because of the ease with which it may be inadvertently introduced into the GaAs during crystal growth as well as various subsequent device processing steps, an understanding of the behavior of hydrogen in the semiconductor is vital. A study of the interaction of hydrogen with the various defects and impurities present in the GaAs also helps in our overall understanding of the complex behavior of the defects and impurities within the material.

There is general consensus that hydrogen may interact in various ways with the host matrix. (i) As an isolated interstitial, atomic hydrogen is mobile in GaAs and may rapidly diffuse through the lattice at elevated temperatures<sup>2</sup>; (ii) hydrogen will readily passivate many electrically active impurities and defects in GaAs through the removal of their associated energy levels from the band gap; (iii) hydrogen has also been found to be responsible for the formation of new electrically active metastable deep levels in GaAs<sup>3</sup>; (iv) hydrogen may form extended precipitates and platelets in GaAs<sup>4</sup>; and (v) theoretical studies<sup>5-8</sup> have predicted that a stable form of hydrogen in GaAs will be the  $H_2$  molecule, positioned at the interstitial tetrahedral ( $T_{Ga}$ ) site nearest the Ga atoms within the lattice. Being presumably electrically neutral and infrared inactive, however, experimental evidence for the presence of  $H_2$  molecules in GaAs has proved to be difficult to obtain (see Table I).

Recently, Vetterhöffer, Wagner, and Weber<sup>9</sup> reported the first experimental evidence for isolated  $H_2$  molecules in hydrogen plasma-treated GaAs. Using Raman spectroscopy at 77 K, they measured a line at 3925.9  $cm^{-1}$ , which they attributed to the vibrational mode of the isolated  $H_2$  molecule at the  $T$  site. Exposing the samples to a deuterium plasma resulted in the expected isotope shift of the Raman line to 2842.6  $cm^{-1}$ , while treatment in a plasma containing a 1:1 mixture of  $H_2:D_2$  yielded three Raman lines due to  $H_2$ ,  $D_2$ , and HD molecules. They were also able to measure the para and ortho modes related to the lowest energy rotational quantum states  $J=0$  and  $J=1$  for the  $H_2$  molecule, respectively.

We have subsequently reported experimental evidence for interstitial  $H_2$  molecules in hydrogenated crystalline Si.<sup>10</sup> Raman studies at room temperature showed a vibrational excitation for the isolated  $H_2$  molecule in Si at 3601  $cm^{-1}$ . This is more than 500  $cm^{-1}$  lower than the well known value of

4161  $cm^{-1}$  for gaseous  $H_2$ .<sup>11</sup> This downward shift in frequency therefore confirms recent calculations<sup>7,8,12</sup> for the vibrational frequency of the  $H_2$  molecule trapped within the lattice of the semiconductor.

In theoretical studies on hydrogen in GaAs,<sup>5-8</sup> it was found that the  $H_2$  molecule would be stable at the  $T_{Ga}$  site, when oriented along the  $\langle 111 \rangle$  axis. The calculations, however, also indicated that very little energy was required to rotate the molecule. In this paper, we first show that the Raman line associated with the  $H_2$  molecule in GaAs can be measured at room temperature. We also examine the temperature dependence of the  $H_2$  Raman line in GaAs, and compare the results with those obtained for Si. Finally, we investigate the possible effect of uniaxial stress on the  $H_2$  line in GaAs, in order to shed more light on the configuration of the molecule in the matrix.

Semi-insulating (SI) undoped GaAs as well as conducting  $n$ -type (Te-doped) and  $p$ -type (Zn-doped) GaAs, all grown by the horizontal Bridgman (HB) technique, were examined in this study. Hydrogen was introduced into the wafers by exposing them to a remote dc hydrogen plasma at typically 250 °C for up to 8 h. The samples were mounted on a heater stage located downstream from the plasma. The hydrogen pressure was held constant at 1.5 mbar. For some of the samples the hydrogen atmosphere was replaced by either deuterium, or a mixture consisting of  $H_2:D_2$  (1:1).

Raman measurements were performed at various temperatures, with the sample mounted in a liquid helium exchange gas cryostat. For excitation, the 413 nm line of a  $Kr^+$  laser was focussed onto the sample. The laser intensity was typically 150 mW. The backscattered light, not analyzed for its

TABLE I. List of the reported Raman frequencies for interstitial  $H_2$  in GaAs, together with data for  $H_2$  in Si as well as  $H_2$  in the gas phase for comparison.

Matrix	$H_2$ ( $cm^{-1}$ )	$D_2$ ( $cm^{-1}$ )	HD ( $cm^{-1}$ )	Reference
GaAs (295 K)	3911	2827	3429	This work
GaAs (77 K)	3934.1	2842.6	3446.5	9
GaAs (theory)	3704			7
GaAs (theory)	3824			8
Si (295 K)	3601	2622		10
$H_2$ (gas)	4161.1	2993.6	3632.1	11

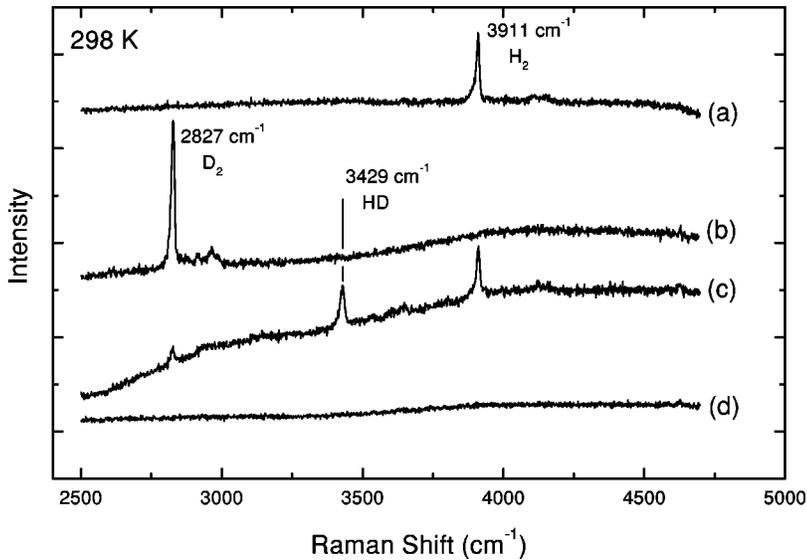


FIG. 1. Room temperature Raman spectra of GaAs, after exposure at 250 °C for 8 h to (a)  $H_2$  plasma, (b)  $D_2$  plasma, (c)  $H_2:D_2$  (1:1) plasma, and (d) no plasma.

polarization, was dispersed with a 0.3 m single grating spectrometer and detected with a cooled Si-CCD detector array. Appropriate holographic notch filters were used to reduce the scattered laser light.

Figure 1 [spectrum (a)] shows a room temperature Raman spectrum of a hydrogen plasma treated Zn-doped ( $9 \times 10^{16} \text{ cm}^{-3}$ ) GaAs sample. The spectrum is dominated by a single line at  $3911 \text{ cm}^{-1}$ . The exposure of a similar GaAs sample to a deuterium plasma resulted in the expected isotopic shift of the Raman line to  $2827 \text{ cm}^{-1}$  [spectrum (b)], while a plasma containing 1:1  $H_2:D_2$  mixture produced three Raman lines at  $3911$ ,  $2827$ , and  $3429 \text{ cm}^{-1}$  [spectrum (c)]. The peak at  $3911 \text{ cm}^{-1}$  is therefore associated with the vibrational mode of the isolated  $H_2$  molecule in the GaAs, while the lines at  $2827$  and  $3429 \text{ cm}^{-1}$  are due to vibrational modes of isolated  $D_2$  and HD molecules, respectively. Spectrum (d) indicates that none of these Raman lines were present in the material before plasma treatment. It may be noted that in contrast to the previous work of Vetterhöffer *et al.*<sup>9</sup> we have found no difference in the Raman intensities of the  $H_2$  molecule in *n*- or *p*-type GaAs.

The linewidth of the measured  $H_2$  Raman line at room temperature is about  $10 \text{ cm}^{-1}$ . It is therefore not possible to resolve the  $Q_1(1)$  (*ortho*- $H_2$ ) and the  $Q_1(0)$  (*para*- $H_2$ ) modes of the vibrational Raman lines at room temperature, which are separated by  $5.9 \text{ cm}^{-1}$  in the case of gaseous  $H_2$ .<sup>11</sup> As the ratio of *ortho*- $H_2$  to *para*- $H_2$  is approximately 3:1 for  $H_2$  gas at room temperature,<sup>13</sup> however, we would expect that the major contribution to the measured Raman line of  $3911 \text{ cm}^{-1}$  comes from the  $Q_1(1)$  mode of the vibrational frequency. This is consistent with measurements at lower temperatures, to be discussed below.

Figure 2 shows the  $H_2$  Raman mode for H plasma treated GaAs, measured at three different temperatures. For temperatures below  $\sim 100 \text{ K}$ , the  $Q_1(0)$  mode becomes visible as a small peak on the high frequency side of the dominant  $Q_1(1)$  peak. It was not possible to fully resolve the  $Q_1(0)$  line, due to the resolution of the spectrometer. The frequency splitting of the  $Q_1(1)$  and  $Q_1(0)$  lines is  $8.0 \text{ cm}^{-1}$ , in agreement with the results of Vetterhöffer *et al.*,<sup>9</sup> while the ratio of the intensities is approximately 2.5:1. Due to the absence of strong nuclear spin-flip processes, the conversion of

*ortho*- $H_2$  to *para*- $H_2$  is known to be a slow process at cryogenic temperatures (of the order of many days).<sup>13</sup> The same intensity ratio of 3:1 is therefore expected for all temperatures under investigation in this study.

It is also seen in Fig. 2 that at 8 K the  $H_2$  Raman peak occurs at a higher frequency than at room temperature. This effect is shown more clearly in Fig. 3, which indicates the measured  $H_2$  peak position as function of temperature. Also included is the reported value of Vetterhöffer *et al.*<sup>9</sup> for the

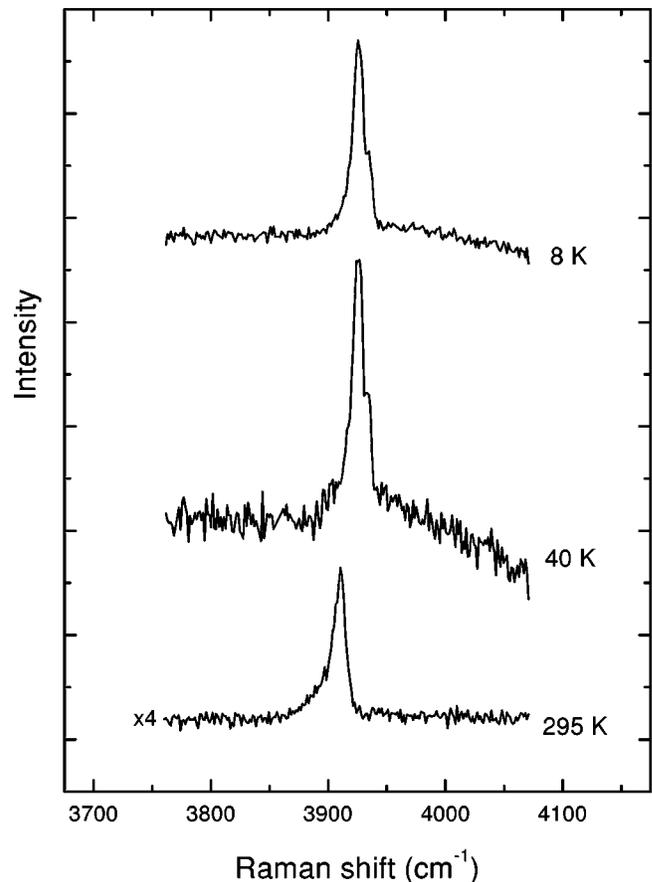


FIG. 2. Raman spectra of the  $H_2$  vibrational excitation in hydrogenated GaAs at different temperatures. The resolution of the spectrometer was  $5 \text{ cm}^{-1}$ .

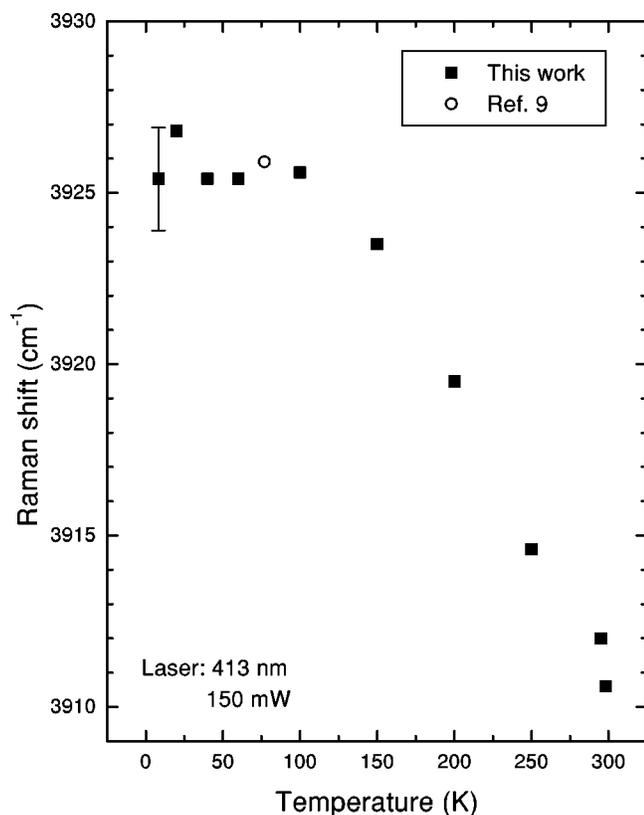


FIG. 3. Temperature dependence of the  $H_2$  Raman peak position in GaAs.

$H_2$  peak at 77 K. At 8 K the  $H_2$  Raman peak occurs at  $3925.4 \text{ cm}^{-1}$  and remains reasonably constant until  $\sim 100 \text{ K}$ , above which it progressively decreases by about  $14 \text{ cm}^{-1}$  to the room temperature value of  $3911 \text{ cm}^{-1}$ . This may be explained in terms of an increase in the bond length of the molecule: As the sample temperature is increased, the increased charge density surrounding the molecule leads to a weakening of the bond and a corresponding decrease in the vibrational frequency.

In order to study the alignment of the  $H_2$  molecule at the  $T_{\text{Ga}}$  site in more detail, uniaxial stress measurements were performed on GaAs crystals cut to dimensions of  $2.0 \times 2.5 \times 7.5 \text{ mm}^3$ , with the long side being aligned with one of the major axes [001], [110], or [111]. The stress on the sample in the cryostat was applied by means of a push rod controlled by compressed gas. The force on the sample was measured with a pressure sensor mounted on the push rod. The maximum stress applied was 0.4 GPa. The incident laser beam was polarized either parallel or perpendicular to the major axis of the sample. Stress measurements at 60 K

failed to produce any splitting of the  $H_2$  Raman line, for the [001], [110], or [111] aligned GaAs samples. According to Kaplyanskii,<sup>14</sup> a defect having tetrahedral symmetry will not exhibit polarized splitting of the frequency for [001] stresses, but both [110] as well as [111] stresses will cause the frequency to split into two components of equal intensities. This has indeed been measured for hydrogen related defects in Si that have tetrahedral symmetry.<sup>15</sup> The lack of splitting of any of the Raman lines under uniaxial stress again indicates that the  $H_2$  molecule is isolated and free to rotate at the  $T_{\text{Ga}}$  site within the GaAs matrix. The present results measured at 60 K therefore confirm the theoretical calculations indicating that the rotational barrier is very small. It must be mentioned that we were not able to detect the Raman line  $S_0(1)$  associated with rotation of the molecule. This is most probably due to the fact that its expected frequency (around  $500 \text{ cm}^{-1}$ ) would lie in the range of the GaAs phonon line, and that its intensity would be relatively low.

Finally, it is interesting to compare the present results with those recently obtained for H-passivated Si<sup>10</sup>. For both semiconductors we find that the confinement of the isolated  $H_2$  molecule at the interstitial site within the host matrix results in a dramatic decrease in the vibrational frequency from the value for  $H_2$  in free space. This downward shift in frequency is greater for Si, due to the smaller lattice constant which leads to a stronger interaction between the  $H_2$  molecule and the host Si atoms. Both materials show a similar variation in vibrational frequency of the  $H_2$  line between 10 K and room temperature. One major difference, however, is that for GaAs it is possible to resolve the  $Q_1(1)$  and  $Q_1(0)$  modes, indicating that the molecule can freely rotate, while for Si the  $H_2$  mode remains a single Raman line, in agreement with the calculations of Hourahine *et al.*<sup>12</sup> Furthermore, the vibrational lines measured for  $H_2$  in GaAs have been found to be quite stable with time, while the vibrational lines for  $H_2$  in Si have shown an hitherto unexplained decrease in intensity with time, the rate of which is dependent on the intensity of the incident laser beam.<sup>16</sup> We conclude therefore that in the case of GaAs, the isolated  $H_2$  molecule is stable at the interstitial site, showing no sign of diffusion under laser excitation.

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\*Present address: Department of Physics, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa.

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