Isolated Hydrogen Molecules in GaAs

J. Vetterhöffer,¹ J. Wagner,² and J. Weber¹

¹Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-70506 Stuttgart, Germany

²Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastrasse 72, D-79108 Freiburg i. Br., Germany

(Received 21 June 1996)

Molecular hydrogen was directly observed in crystalline GaAs by Raman spectroscopy. At T = 77 K, GaAs samples that have been exposed to a hydrogen/deuterium plasma exhibit four vibrational lines at 2842.6, 3446.5, 3925.9, and 3934.1 cm⁻¹, respectively. With a pure hydrogen plasma only the two high frequency lines can be seen and with a pure deuterium plasma only the lowest frequency is observed. We attribute these frequencies to the rovibrational modes of isolated interstitial D₂, HD, and H₂ molecules, respectively. [S0031-9007(96)01995-3]

PACS numbers: 71.55.Eq, 33.20.Fb, 78.30.Fs

Hydrogen is an important impurity in many semiconductors because of its tendency to form complexes with most crystal defects and impurities. In combination with its presence during crystal growth and processing, hydrogen has gained both fundamental and technological interest [1–5]. There is now general agreement that hydrogen exists in various forms in the crystal [5–8]: (a) isolated hydrogen interstitials, (b) hydrogen bonded to crystal defects or impurity atoms, (c) the H₂ and H₂^{*} dimers, and (d) extended hydrogen precipitates or platelets.

Extensive experimental and theoretical work on hydrogen in silicon has led to a more detailed understanding of its properties in this material compared to all other semiconductors. Two kinds of hydrogen dimers are predicted by theory: H₂ molecules roughly centered at a T site and the "bond-centered/antibonding" pair H₂^{*}. The latter was recently identified in proton implanted silicon [9]. It consists of two hydrogen atoms, one sitting close to a bond-centered site and the other at an antibonding site $(Si - H \cdots Si - H)$. Molecular hydrogen was never unambiguously identified in crystalline silicon. Stallinga et al. [10] reported the NL52 EPR center in silicon after hydrogen implantation, which they attributed to a charged H₂ molecule. However, theoretical considerations show that both H_2^- and H_2^+ are not stable in silicon [8,11]. Further experimental evidence that NL52 does not correspond to isolated H₂ but possibly is due to a larger hydrogen complex comes from ENDOR measurements [10,12].

In contrast to crystalline silicon, hydrogenated amorphous silicon can contain serveral at. % of hydrogen. In that case, the existence of hydrogen microbubbles was shown by different techniques such as nuclear magnetic resonance, calorimetry, and infrared (IR) absorption [13]. Weak IR absorption signals lead to the conclusion that part of the hydrogen is present in microvoids as H_2 gas at very high pressures [14], but isolated molecules were not reported.

Hydrogen molecules at normal pressure are IR inactive due to their lack of dipole moment, but they can be studied by Raman scattering. Raman investigations of gaseous H₂, D₂, and HD [15] show rovibrational lines corresponding to the Raman selection rules $\Delta v = 0, \pm 1$ and $\Delta J = 0, \pm 2$ (v = 0, 1, 2, ... denotes the vibrational quantum number and J = 0, 1, 2, ... is the rotational quantum number) [16]. Extended studies were also performed on liquid and solid hydrogen [17] and on H₂, D₂, and HD molecules trapped in matrices like silica [18], solid Ar, Kr, Xe [19], O₂, or N₂ [20,21].

In this Letter we present the first experimental identification of molecular hydrogen in crystalline semiconductors. The Raman spectra of hydrogenated and deuterated GaAs reveal the characteristic vibrational modes of H_2 , D_2 , and HD complexes.

We examined GaAs samples of four different types. Tedoped liquid encapsulated Czochralski (LEC) grown GaAs $(n \approx 1 \times 10^{17} \text{ cm}^{-3})$, semi-insulating (SI) HB (horizontal Bridgeman) grown GaAs ($n \sim 1 \times 10^{15} \text{ cm}^{-3}$), Zn-doped HB GaAs ($p \approx 4.5 \times 10^{16} \text{ cm}^{-3}$), and "low temperature" (LT) GaAs samples were all cut from wafers. The latter consists of a 2 μ m thick layer of GaAs that was grown by molecular beam epitaxy (MBE) on a semiinsulating substrate at $T_s = 300$ °C. As a consequence of this low growth temperature, excess arsenic is incorporated into the lattice at interstitial sites or as arsenic antisite defects (in our samples [As_{Ga} $\approx 6 \times 10^{19} \text{ cm}^{-3}$], as measured by near IR absorption; see, for example, Ref. [22] for more details on this material). All the samples were exposed to a remote dc hydrogen plasma for 3-12 h at a temperature of 200 °C or 254 °C. Some of the samples were then partially etched in a $NH_4OH/H_2O_2/H_2O_3$ solution, removing 0.7 \pm 0.1 μ m from the plasma treated surface. The rest of the sample was protected by a photoresist. Raman measurements were then performed at T = 77 K on both the etched and nonetched areas. For excitation, the 3.00 eV line of a Kr-ion laser was used. From the absorption coefficient α of GaAs [23] the estimated probing depth $\frac{1}{2\alpha}$ is about 10 nm. The excitation power of 200 mW was focused on a $\sim 100 \ \mu m$ spot with polarization parallel to a [100] direction. The backscattered light from a (100) surface was analyzed with



FIG. 1. Low temperature (T = 77 K) Raman spectra of three samples after different plasma treatments. (a) SI-GaAs, 8 h H₂ plasma treatment at T = 254 °C, (b) LT-GaAs, 3 h D₂ plasma treatment at T = 200 °C, (c) LT-GaAs, 8 h 50% H₂/50% D₂ plasma treatment at T = 200 °C. Residual laser plasma lines are indicated by stars (*). Spectral resolution was set to 6 cm⁻¹.

a triple monochromator (without polarizer) and detected with a liquid-nitrogen-cooled silicon charge-coupled device (CCD) detector array. Spectral resolution was set to 6 cm^{-1} (2 cm⁻¹ for the high resolution spectrum).

After a hydrogen/deuterium plasma treatment, new sharp Raman lines are observed in all four GaAs samples. No signal is found in an untreated reference sample. Using a pure H₂ plasma, a doublet [labeled "H2" in Fig. 1(a)] is observed. It is replaced by a single line at lower frequency [labeled "D2" in Fig. 1(b)] when using a pure D₂ plasma instead. Finally, using a mixture of 50% H₂ and 50% D₂ for the plasma, these lines plus an additional one at an intermediate frequency [labeled "HD" in Fig. 1(c)] appear in the spectrum. These lines are seen in all substrates used in this study, but they are only very weak in the *p*-type sample (Fig. 2).

We interpret these lines as vibrational excitations of isolated H_2 , D_2 , and HD molecules, respectively. Table I summarizes the observed lines together with the corresponding transitions found in different matrices. The mass



FIG. 2. Low temperature (T = 77 K) Raman spectra of four different GaAs samples. The samples were exposed for 8 h at 200 °C to a 50% H₂/50% D₂ plasma. Residual laser plasma lines are indicated by stars (*). Spectral resolution was 6 cm⁻¹.

dependence is almost the same for all materials, except that our frequencies are $100-200 \text{ cm}^{-1}$ lower. This would suggest a somewhat weaker molecular bond than in free space. The frequency ratio *r* of H2 by D2 is in all cases close to $\sqrt{2}$, the value that would be expected for a free, harmonic oscillation of two hydrogen (deuterium) atoms.

Figure 3 shows the H2 line measured with a higher resolution of 2.0 cm^{-1} . It clearly shows a second, weaker component at 3934.1 cm⁻¹. No splitting is observed for the HD and D2 lines. The linewidths of H2, HD, and D2 are 3, 8, and 7 cm⁻¹, respectively. This small value of the linewidth reflects a weak perturbation of the oscillator by its environment. Within experimental error, all our samples exhibit the same splittings and linewidths.

In order to check the depth of the Raman signal, 0.7 μ m from the sample surface was chemically removed and the measurement repeated. In all four materials the signal had disappeared. However, secondary ion mass spectroscopy measurements confirm that hydrogen is present much deeper in the sample (several μ m). The profile exhibits a very high hydrogen concentration of $\sim 1 \times 10^{19}$ –1 $\times 10^{20}$ cm⁻³ close to the surface (<0.1 μ m) and a plateau

TABLE I. Summary of the observed Raman transitions Q(0) of H₂, D₂, and HD molecules in different environments. $r = \nu_{H_2}/\nu_{D_2}$ denotes the frequency ratio of the H₂ and D₂ vibration.

Matrix	$H_2 (cm^{-1})$	$D_2 (cm^{-1})$	HD (cm^{-1})	r	Reference
GaAs	3934.1	2842.6	3446.5	1.381	This work
H_2 (gas)	4161.13	2993.55	3632.06	1.3900	[15]
H ₂ (liquid)	4153.78	2987.99	3623.65	1.3902	[17]
H_2 (solid)	4151.8	2982.46	3621.85	1.3921	[17]
Solid Ar	4142.1	2979.2	3615.4	1.3903	[19]
Solid Kr	4132.4	2972.5	3607.0	1.3902	[19]
Solid Xe	4123.4	2966.9	3600.5	1.3898	[19]
Solid N ₂	4145.5	2980.7	3617.7	1.3908	[21]
Solid O ₂	4147	2986.0		1.389	[20]



FIG. 3. Splitting of the H2 line measured with a spectral resolution of 2 cm⁻¹ on a LT-GaAs sample at T = 77 K. The samples were exposed for 8 h at 200 °C to a 50% H₂/50% D₂ plasma.

region with a ~ 10 times lower concentration at greater depth. These profiles are very similar to those reported elsewhere [24,25]. This shows that molecules are detected only in those regions where the hydrogen concentration reaches very high values.

It would be interesting at this point to estimate the concentration of molecular hydrogen that we detect by our Raman measurements from the signal intensity, the probing depth, and the Raman cross section of H₂. However, such an estimation would be rather doubtful because the differential Raman cross section $d\Omega/d\sigma$ of H₂ is known only for hydrogen gas [26]. For molecules in a solid matrix the Raman scattering is considerably enhanced due to the local field effect [27,28]. There are several approaches in the literature to calculate the local field, but no conclusion can be made about which of them is the most appropriate (see, for example, Ref. [13] for a discussion of the Si-H absorption strength in amorphous silicon). While for transmission measurements the absorption intensity is proportional to the square of the local electric field E_{eff} only, the Raman cross section is proportional to the fourth power of $E_{\rm eff}$ [27,28]. The calculated enhancement factor L ranges from $L \approx 6$ (Onsager's model) to $L \approx 2800$ (Lorentz local field) [29]. This considerable error makes a quantitative analysis of the measured Raman intensity meaningless.

From theory, H_2 molecules are expected to be stable at (or close to) a tetrahedral (T) interstitial site [5,7]. The activation energy for diffusion is calculated to be high, whereas the barrier for rotation is small. The bond length is found to be within a few percent of the free molecule value (0.75 Å [15]).

These results suggest a possible explanation for the observed 8 cm⁻¹ splitting of the H2 line, if one assumes a rotational motion of the H₂ molecules. At low temperatures, only the lowest accessible molecular state is populated. This state depends on the molecule's total nuclear

spin I. I can be either 0 or 1 for H_2 (spin one-half system) and 0, 1, or 2 for D_2 (spin one system). For H_2 with I = 0 ("para-H₂") and D₂ with I = 0 or 2 ("ortho-D₂") the lowest accessible state is the ground state v = 0 and J = 0, but for H₂ with I = 1 ("ortho-H₂") and D₂ with I = 1 ("para-D₂") the ground state is forbidden by symmetry (homonuclear molecule). In this case, only the higher lying state v = 0 and J = 1 is populated. The equilibrium concentration of the ortho and para modification is temperature dependent. In the high temperature limit $kT \gg hcB$ (B is the rotational constant) the ratio equals $g_{\rm ortho}/g_{\rm para}$, where g is the nuclear statistical weight of the particular modification [16]. For H₂, $B \approx 60 \text{ cm}^{-1}$ [15] so that at room temperature the ortho/para ratio is $(2 \times 1 + 1)/(2 \times 0 + 1) = 3:1$. For D₂, $B \approx 30$ cm⁻¹ and the room temperature ortho/para ratio equals 2:1. The ortho-para conversion is usually a very slow process with a time constant (in nonparamagnetic matrices) of many days [16]. As a consequence, the room temperature distribution is virtually maintained during a rapid cooling down of the sample.

Then, two Raman transitions are observed: $(v = 0/J = 0) \rightarrow (v = 1/J = 0)$ [Q(0) line] and $(v = 0/J = 1) \rightarrow (v = 1/J = 1)$ [Q(1) line]. Because of the rovibrational coupling, they have slightly different energies. Their intensities directly give the para/ortho ratio. For hydrogen gas, Q(0) is 5.9 cm⁻¹ higher in frequency than Q(1), and this value is virtually unchanged for hydrogen molecules in solid rare gas matrices [20]. This frequency splitting and the expected intensity ratio of 3:1 are both consistent with the observed values of the H2 line (Fig. 3). For deuterium gas however, Q(0) is only 2.1 cm⁻¹ higher in frequency than Q(1). The expected splitting of the D2 line is thus comparable to our highest spectral resolution and smaller than the linewidth. Therefore, it can unfortunately not be resolved.

In conclusion, our results demonstrate the existence of isolated hydrogen molecules in GaAs. In agreement with theory, these molecules are weakly perturbed by the host and rotate easily. This follows from the sharpness of the lines and from the observation of the first rotational state of the H_2 molecules. The influence of the GaAs matrix is reflected by a considerable frequency shift to lower values as compared to molecules in free space or in solid gas matrices.

We are grateful to K. Köhler for supplying the LT-GaAs samples and to Professor H.-J. Queisser for his continued support and interest. We ackowledge the technical assistance of H.-W. Krause. J. W. thanks Professor P. Koidl for his continued support.

Hydrogen in Semiconductors, edited by J. I. Pankove and N. M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic Press, San Diego, 1991).

- [2] S.J. Pearton, J.W. Corbett, and M. Stavola, *Hydrogen* in Crystalline Semiconductors (Springer-Verlag, Berlin, 1992).
- [3] S.J. Pearton, Mater. Sci. Forum 148,149, 393 (1994).
- [4] S.K. Estreicher, Mater. Sci. Eng. **R14**, 319 (1995).
- [5] L. Pavesi and P. Giannozzi, Phys. Rev. B 46, 4621 (1992).[6] B. Holm, K. Bonde Nielsen, and B. Bech Nielsen, Phys.
- Rev. Lett. **66**, 2360 (1991).
- [7] S.J. Breuer, R. Jones, P.R. Briddon, and S. Öberg, Phys. Rev. B 53, 16289 (1996).
- [8] S. K. Estreicher, M. A. Roberson, and Dj. M. Maric, Phys. Rev. B 50, 17018 (1994).
- [9] J.D. Holbech, B.Bech Nielsen, R. Jones, P. Sitch, and S. Öberg, Phys. Rev. Lett. **71**, 875 (1993).
- [10] P. Stallinga, T. Gregorkiewicz, C. A. J. Ammerlaan, and Yu. V. Gorelkinskii, Phys. Rev. Lett. 71, 117 (1993).
- [11] K. L. Brower, S. M. Myers, A. H. Edwards, N. M. Johnson, C. G. Van de Walle, and E. H. Pointdexter, Phys. Rev. Lett. 73, 1456 (1994).
- [12] P. Stallinga, T. Gregorkiewicz, and C. A. J. Ammerlaan, Phys. Rev. Lett. 73, 1457 (1994).
- [13] Y.J. Chabal and C.K.N. Patel, Rev. Mod. Phys. 59, 835 (1987).
- [14] Y.J. Chabal and C.K.N. Patel, Phys. Rev. Lett. 53, 210 (1984).
- [15] B. P. Stoicheff, Can. J. Phys. 35, 730 (1957).
- [16] G. Herzberg, Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules (Van Nostrand Reinhold,

New York, 1950).

- [17] S. S. Bhatnagar, E. J. Allin, and H. L. Welsh, Can. J. Phys. 40, 9 (1962).
- [18] C. M. Hartwig and J. Vitko, Jr., Phys. Rev. B 18, 3006 (1978).
- [19] M. E. Alikhani, B. Silvi, and J. P. Perchard, J. Chem. Phys. 90, 5221 (1989).
- [20] K. D. Bier, H. J. Jodl, and H. Däufer, Can. J. Phys. 66, 708 (1988).
- [21] M. E. Alikhani and J. P. Perchard, J. Phys. Chem. 94, 6603 (1990).
- [22] D.C. Look, Thin Solid Films 231, 61 (1993).
- [23] M. Cardona and G. Harbeke, J. Appl. Phys. 34, 813 (1963).
- [24] R. Rahbi, D. Mathiot, J. Chevallier, C. Grattepain, and M. Razeghi, Physica (Amsterdam) 170B, 135 (1991).
- [25] G. Roos, N. M. Johnson, C. Herring, and J. Walker, Mater. Sci. Forum 143–147, 933 (1994).
- [26] H. W. Schrötter and H. W. Klöckner, in *Raman Spectroscopy of Gases and Liquids*, edited by A. Weber (Springer-Verlag, Berlin, 1979).
- [27] D. L. Dexter, in Solid State Physics, Advances in Research and Applications, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 6.
- [28] G. Eckhardt and W. G. Wagner, J. Mol. Spectrosc. 19, 407 (1966).
- [29] L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).