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Interstitial H_2 in germanium by Raman scattering and *ab initio* calculations

M. Hiller,[1] E. V. Lavrov,[1] J. Weber,[1] B. Hourahine,[2] R. Jones,[3] and P. R. Briddon[4]
[1]*Institute of Applied Physics, TU Dresden, 01062 Dresden, Germany*
[2]*Department of Physics, University of Strathclyde, John Anderson Building, 107 Rottenrow, Glasgow G4 0NG, United Kingdom*
[3]*School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom*
[4]*School of Natural Sciences, Herschel Building, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, United Kingdom*
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Single-crystalline germanium wafers exposed to hydrogen and/or deuterium plasma are studied by means of Raman scattering. The Raman frequencies are compared to results of *ab initio* calculations. For samples treated with pure hydrogen, Raman measurements performed at a temperature of 80 K reveal two sharp lines at 3826 and 3834 cm^{-1} with an intensity ratio of 3:1, which are assigned to ortho- and para-H_2 trapped at the interstitial *T* site of the lattice.

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Molecular hydrogen in semiconductors was predicted to be stable by theory more than 20 years ago.[1,2] Due to the technological importance of Si and GaAs most of the H_2 studies have been performed for these materials. Today, it is known that H_2 can be trapped at various sites of the semiconductor lattice: (*i*) at the interstitial *T* site in Si (Refs. 3–5) and GaAs,[6,7] (*ii*) at hydrogen induced platelets in Si (Refs. 5, 8, and 9) and Ge,[10,11] (*iii*) at voids in Si (Refs. 12 and 13) and GaAs,[7] and (*iv*) at interstitial oxygen in Si.[3,14,15]

Interest in hydrogen within Ge comes from the fact that this is the only atmosphere suitable for the growth of high purity Ge single crystals.[16] Very recently, hydrogen-induced platelets were identified in hydrogen-plasma-treated Ge by means of Raman scattering, and it was shown that molecular hydrogen can be trapped within these platelets as well.[11]

In addition to molecular H_2, another type of hydrogen dimer is known to exist in elemental semiconductors.[17–19] It is labeled as H_2^* and consists of two hydrogen atoms, one sitting close to a bond-centered site and the other one at an antibonding site. Theory predicts that the relative stability of interstitial H_2 as compared to H_2^* grows with the host lattice constant for the group IV elements.[20,21] That is, H_2 is expected to be the ground state of hydrogen in Ge. Nonetheless, interstitial H_2 in Ge has never been observed.

Here we report on a combined Raman scattering and theoretical study of hydrogen-plasma-treated Ge. It is shown that interstitial H_2 in Ge is formed during the plasma treatment and results in Raman signals at 3826 and 3834 cm^{-1}. This agrees with a calculated estimate that the vibrational mode of H_2 in Ge should fall at ~ 3713 cm^{-1}.

Germanium samples used in this study were *p*-type, Ga-doped, *Cz* (100) wafers with a resistivity of 25 Ω cm, purchased from Umicore. The samples were hydrogenated in a remote dc hydrogen plasma for 8 h at a temperature of 175 °C. The gas pressure was held at 1.5 mbar. For the isotope substitution experiments hydrogen was replaced by either pure deuterium or a mixture of H:D (50:50).

Raman measurements were performed in a pseudo-backscattering geometry using the 532 nm line of a Nd:YVO_4 laser for excitation. With the absorption coefficient $\alpha = 5.57 \times 10^5$ cm^{-1} of Ge for the given wavelength, the estimated probing depth $1/2\alpha$ is about 9 nm.[22] The incident laser beam made an angle of 40° with the sample normal. The laser power on the sample surface was ~ 270 mW. To reduce overheating of the sample, the excitation light was focused on a spot size of about 50 $\mu m \times 5$ mm using a cylindrical lens. The backscattered light was analyzed using a single grating spectrometer and a liquid-nitrogen-cooled Si CCD detector array. Spectral resolution was set to 4 cm^{-1}. Integration time for the spectra was 30 h. The measurements were performed with the sample mounted in a cold finger cryostat using liquid helium for cooling. The temperature within the excitation area was estimated from the Stokes to anti-Stokes ratio of the Ge phonon line to be approximately 80 K.

Figure 1 shows Raman spectra of Ge samples after exposure to hydrogen and/or deuterium plasma. The reference spectra of a virgin sample in the respective spectral regions are given for comparison. After treatment with a pure hydrogen plasma, a doublet with two sharp Raman components at 3826 and 3834 cm^{-1} is observed. When hydrogen is substituted by deuterium, this doublet is replaced by a single line which is shifted downwards in frequency by approximately a factor of $\sqrt{2}$ to 2782 cm^{-1}, thus showing that the signals originate from stretch local vibrational modes (LVMs) of hydrogen. Note that the apparent splitting of the 2782 cm^{-1} line in Fig. 1 is an artefact of the CCD.

We assign the Raman signals at 3826 and 3834 cm^{-1} to ortho (nuclear spin 1) and para (nuclear spin 0) interstitial H_2 trapped at the *T* site within the Ge host lattice. Because of symmetry requirements for the total wave function, for ortho (para) H_2 the lowest possible value for the rotational quantum number is $J=1$ ($J=0$).[23] The intensity ratio of approximately 3:1 (Ref. 6) for these two lines and the value of the splitting of 8 cm^{-1} (Ref. 24) strongly support this assignment. The expected ortho-para splitting of the D_2 species equals 2.5 cm^{-1}.[24] This value is well below our resolution limit of 4 cm^{-1}, which explains why the D_2 spectrum reveals only one component of the molecule.

No definite Raman signal originating from HD molecules could be observed in our samples when using a mixed H:D plasma. From the observed frequencies for the LVMs of H_2 and D_2, the expected vibrational frequency of the HD mol-

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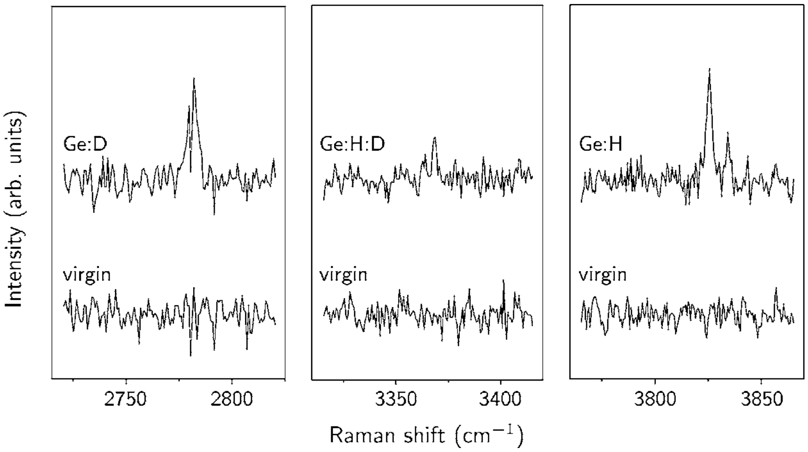

FIG. 1. Raman spectra of (100)-Ge after exposure for 8 h at 175 °C to a D-, H:D(50:50)-, and H-plasma, and the corresponding reference spectra of a virgin sample. Integration time was 30 h. Spectra are baseline corrected and offset vertically for clarity.

ecule can be roughly estimated to be $\sim$3360 cm^{-1}.[24] Indeed, there is a hint for a signal positioned at 3368 cm^{-1} in the spectrum of a sample after exposure to an H:D plasma, but it is too weak for a definite assignment. For equal concentrations of H and D isotopes in the sample, the ratio of the concentrations of H_2, HD, and D_2 should be 1:2:1. Since the intensities of the Raman lines are proportional to μ^{-1}, where μ is the reduced mass of the scattering species,[25] the expected intensity of the HD line should be 3/8 of the H_2 line intensity. Even though, this should still be within the detection limit of our Raman setup. A possible explanation for the weakness of the HD signal will be given below.

From thermal effusion experiments it is known that the maximum deuterium content in Ge deuterated from plasma is about one order of magnitude less than for similarly treated Si.[26] Apart from that, the probing depth of our laser is only 9 nm, which is a factor of about 45 less than that for Si for the same wavelength.[22] Altogether, this increased the required integration time to 30 h and makes further experimental investigation of the H_2 properties in Ge, for instance thermal stability, an extremely hard task. Infrared absorption measurements performed as part of this work on Ge samples annealed at 900 °C in sealed quartz ampoules containing H_2 or D_2 gas did not reveal any signals in the corresponding spectral regions either.

The observed modes were compared against first-principles density functional results,[27,28] in conjunction with cubic cells of between 64 and 512 atoms. The wave functions of the host material were represented with a real-space contracted Cartesian-Gaussian basis centered on each atom, using two independent contracted groups of four separate exponents (with different contraction coefficients for *s* and *p*) and an additional uncontracted *d* set. The hydrogen used an uncontracted set of 4*s* and *p* functions. The Hartree and Perdew-Wang[29] exchange-correlation energies were calculated using a converged 120 Ryd. plane-wave fitting to the charge density, with a $2\times2\times2$ Monkhorst-Pack *k*-point sampling scheme used to integrate over the band structure.[30] Hartwigsen-Goedecker-Hutter[31] pseudopotentials were used for the semiconductor hosts while a bare proton was used for the hydrogen potential.

All atoms were allowed to relax by a conjugate gradient method. The second derivatives of the energy were found for the H atoms and immediate neighbors, with additional entries in the matrix constructed from a Musgrove-Pople potential, allowing quasi-harmonic vibrational modes to be calculated from the dynamical matrix (further details are given in Ref. 27). The error in the calculated modes between the 216 atom host values presented here and for a 512 atom cell was estimated to be $\sim$3 cm^{-1} by comparing against minimal contracted basis calculations for 64, 216, and 512 cells.

The resulting modes for H_2 in Si, GaAs and Ge are shown in Table I, for statically aligned molecules along [100], [110], and [111] directions. The energy differences between these orientations are negligible ($\sim$5 meV in all host materials shown), and the molecule is then expected to be a free rotor, in agreement with previous calculations. From these statically aligned calculations, an estimate can be made for the vibrational mode of the $J=0$ molecule by taking a weighted average of the static configurations. This leads to modes of $\sim$3713, $\sim$3222, and $\sim$2627 cm^{-1} for interstitial H_2, HD, and D_2 in Ge. The H_2 mode falls $\sim$120 cm^{-1} lower than the observed value; this is also typical of the error in calculated H_2 modes for Si and GaAs. Thus, these results provide additional support for our assignment of the 3826 and 3834 cm^{-1} lines to ortho and para interstitial H_2 at the *T* site in Ge.

However, the calculated values for the molecule at the As surrounded *T* site in GaAs are in somewhat poorer agreement with experiment, $\sim$200 cm^{-1} in the case of H_2. Notice that GaAs is a compound semiconductor and because of this there are two possible interstitial sites for H_2: one with Ga closest neighbors (T_{Ga}), the other one with As atoms nearby (T_{As}). For H_2 in Si, Ge, and at the T_{Ga} site in GaAs, the calculations systematically underestimate the observed frequencies by about 120 cm^{-1}. Following this trend, one would expect the mode for H_2 at the T_{As} site in GaAs to lie around 3950 cm^{-1} rather than the observed 4043 cm^{-1} (Ref. 7). This discrepancy could hint that either the behavior of H_2 when surrounded by anions differs from the other three cases, or that the Raman mode at 4043 cm^{-1} may instead possibly be due to H_2 trapped in some kind of void or platelet.

For Si and GaAs theory predicts that the H_2 molecule at the *T* site is a nearly free rotator.[33–38] Additionally, we find similar behavior in Ge. Experimentally, this results in two stretching LVMs originating from ortho- and para-nuclear spin states which are split by rovibrational coupling.[6] In the case of Si, the para-H_2 Raman signal was shown to be un-

TABLE I. Measured and calculated vibrational modes (cm^{-1}) of H_2 in several host materials. For HD in Si, the 3191.1 cm^{-1} mode originates from a $J=1 \rightarrow J=1$ transition (Ref. 32). Since the calculations use statically aligned molecules, the $\langle 111 \rangle$ alignment has two inequivalent H atoms; the values for both the HD and DH configurations are then given. In GaAs, the calculated energy difference ΔE between H_2 at Ga and As surrounded T sites is found to be $\sim$0.2 eV (experimentally this has been determined to be $\Delta E = 60$ meV, see Ref. 7).

	Si				Ge			
	Expt.[3–5,24,32]	[100]	[110]	[111]	Expt.	[100]	[110]	[111]
H_2	3627	3522.4	3542.3	3544.1	3834	3731.0	3702.9	3702.1
HD	3191.1	3057.1	3075.3	3078.1, 3078.6		3237.2	3213.5	3213.4, 3213.4
D_2	2645	2491.7	2505.7	2507.5	2782	2639.2	2619.3	2618.8
	GaAs-T_{Ga}				GaAs-T_{As}			
	Expt.[6]	[100]	[110]	[111]	Expt.[7]	[100]	[110]	[111]
H_2	3934.1	3813.0	3806.0	3797.9	4043	3838.8	3834.7	3817.6
HD	3446.5	3308.3	3303.0	3303.4, 3289.5	3602	3331.9	3328.4	3311.7, 3316.5
D_2	2842.6	2697.6	2692.6	2687.1	2920	2715.9	2712.9	2700.9

stable against room temperature annealing and band gap illumination.[24,39] This phenomenon was tentatively explained by different diffusivities of the hydrogen molecules in the $J=0$ (para-H_2) and $J=1$ (ortho-H_2) states. Here J is the rotational quantum number. Afterwards, for GaAs it was also shown that para-H_2 is unstable with respect to the bandgap illumination at elevated temperatures and can be seen in Raman spectra only for temperatures below 120 K, which seemed to strengthen the above explanation.[7,39] However, contrary to the Si case, for GaAs both ortho- and para-H_2 anneal out at the same rate, which seemed to contradict the suggestion of different diffusivities of the two species. A possible explanation of this puzzle could be provided by the assumption that the annealing kinetics of H_2 in GaAs might be determined by dissociation rather than diffusion. Comparison with the properties of H_2 in other semiconductors could be useful to elucidate this problem. Unfortunately, the extremely weak Raman signal from H_2 in Ge makes annealing experiments on H_2 impossible.

Even though, the weakness of the HD Raman signal in Ge seems to be in favor of the model of different diffusivities of ortho and para states. Since HD is a hetero-nuclear molecule, the rotational states are no longer restricted by the symmetry of the nuclear spin state, and at low temperature only the $J=0$ state is populated. In Si, the species with $J=0$ was shown to disappear from the Raman spectra preferentially.[24,39] However, the IR study of the formation rate of the O-D_2 complex performed by Stavola *et al.* suggests that para and ortho D_2 have similar diffusivities at room temperature.[40]

Raman measurements of Si after exposure to an H:D (50:50) plasma performed at cold temperatures also could not unambiguously identify a signal related to interstitial HD.[24,39] In contrast, in the Raman studies of Si treated with an H:D (10:90) plasma performed at room temperature by Kitajima *et al.*, a line at 3177 cm^{-1} assigned to interstitial HD in Si was observed.[41] This signal could not be seen after exposure of the sample to an H:D (50:50) plasma. The infrared absorption measurements of Si samples after annealing in an H:D-atmosphere at 1250 °C performed by Chen *et al.* also revealed two lines at 3191.1 and 3265.0 cm^{-1} attributed to rovibrational transitions of interstitial HD.[32] Contrary to the Si case, cold temperature Raman measurements of GaAs samples after exposure to an H:D (50:50) plasma exhibit a relatively strong signal originating from interstitial HD.[6,7,39] As already pointed out above, the possibly differing behavior of interstitial H_2 in different hosts such as Si and Ge on the one hand and GaAs on the other hand could play an important role in explaining this puzzle.

Finally, we comment on the tentative assignment of a Raman line at $\sim$3925 cm^{-1} to interstitial H_2 in Ge in our previous paper.[11] Higher resolution measurements of this signal performed as a part of this work showed that this line does not reveal any ortho-para-splitting and that it is much broader (FWHM$\approx$20 cm^{-1}) than one would expect for interstitial H_2 from the known results on Si and GaAs. Based on this, we propose that the 3925 cm^{-1} line is due to H_2 trapped in some type of void different from the known dominating $\{111\}$ hydrogen-induced platelets.

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