RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 50, NUMBER 4 15 JULY 1994-II

Local hydrogen vibrational modes in GaAs doped with S, Se, and Te

J. Vetterhöffer, J.H. Svensson, and J. Weber
Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-70506 Stuttgart, Germany

A.W.R. Leitch and J.R. Botha
Department of Physics, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, Republic of South Africa

(Received 5 May 1994)

We present a systematic study on the infrared absorption of S-, Se-, and Te-doped metal-organic chemical vapor deposition GaAs layers which were subjected to a prolonged hydrogen plasma treatment. For all donor species, two new vibrational modes are detected at 780.58 and 1512.30 cm^{-1} (GaAs:S); 777.95 and 1507.46 cm^{-1} (GaAs:Se); 771.81 and 1499.93 cm^{-1} (GaAs:Te). In samples treated in a deuterium plasma, the modes attributed to hydrogen are shifted by a characteristic amount. We identify the modes as due to hydrogen group-VI donor stretching and wagging vibrations. The proposed model for the complexes, where the hydrogen is bound in the antibonding position of the nearest Ga atom, accounts for the observed vibrational properties.

It is now well established that a hydrogen plasma treatment can passivate shallow donors in GaAs.[1–3] By exposing n-type GaAs to a hydrogen plasma, the passivation typically extends a few micrometers deep into the material. It has been shown from electrical measurements that the free electron concentration in n-type GaAs doped with the group-IV elements Si, Ge, and Sn, or with the group-VI elements S, Se, and Te, is drastically reduced after such a treatment.[4,5] In an earlier paper by Pearton *et al.*,[4] the reduction of the free carrier concentration, as determined from capacitance-voltage C-V depth profiles, was attributed to the passivation of the donor activity via the association of a single hydrogen or deuterium atom with the donor atom. The hydrogen atom was suggested to be directly bound to the donor atom, so that the extra donor electron is utilized by this bond. The hydrogen atom is then located in an antibonding position with the donor-hydrogen bond along a $\langle 111 \rangle$ direction.

In the case of the hydrogen-passivated group-IV donor Si_{Ga} (the subscript denotes the lattice site of the donor atom), substantial support for this model was found by infrared spectroscopy.[6–8] Two infrared absorption lines are detected and attributed, respectively, to the stretching and the bending localized vibrational mode (LVM) of the Si_{Ga}-H bond. The behavior of these lines under uniaxial stress confirmed the model. Calculations showed that the Si_{Ga}-As bond opposite to the Si-H bond is lengthened. Due to the presence of the hydrogen atom,[10,12–14] the hybridization of the other three Si-As bonds changes from sp^3 to bonds with sp^2 character; the fourth As atom then has a filled lone pair orbital directed towards the Si atom. The bond between the Si donor and the As atom opposite to the Si-H bond is practically broken. Similar absorption lines due to LVM's have been found in Sn-doped GaAs passivated by hydrogen.[9]

Recently, we have reported preliminary results on the vibrational modes of Se-H complexes and suggested a direct bonding of hydrogen to the group-VI donor in an antibonding position.[11] Chang,[10] however, has performed calculations for the S_{As}-H complex which favor the bonding of hydrogen to the next Ga neighbor also in an antibonding position. No calculated vibrational frequencies were given in Ref. 10. The theoretical predictions ask for a systematic study of the different chalcogen-hydrogen complexes in GaAs to identify the exact position of the hydrogen atom. In this communication we will present strong evidence for the model proposed by Chang[10] from the study of the LVM's of S-, Se-, and Te-doped GaAs.

The samples used in this study consist of S- and Se-doped layers grown by metal-organic vapor phase epitaxy and Te-doped layers grown by liquid phase epitaxy on undoped semi-insulating GaAs substrates. The thickness of the different layers varied between 1 and 10 μm with carrier concentrations from $2\times10^{18}\ \text{cm}^{-3}$ to $1\times10^{19}\ \text{cm}^{-3}$. Mechanical polishing of the substrate was performed in order to obtain a wedge of a few degrees to avoid interference from the substrate in the spectra. For passivation, epitaxial layers were exposed for about 50 h to a remote hydrogen or deuterium dc plasma in a parallel plate system with a plate voltage of 1000 V. The samples were mounted on a heater block held at a temperature of 180 °C and placed 10 cm downstream from the plasma with a bias voltage of -320 V, while the pressure was held at 1 mbar. Infrared transmission was measured at normal incidence with a BOMEM DA3.01 Fourier transform spectrometer, equipped with an MCT detector. To avoid mounting stress, the samples were free-standing in the sample compartment of an exchange-gas cryostat.

New sharp LVM's were found in the passivated samples. Absorption, however, was generally very weak, and we never observed the deuterium induced lines in Te-doped GaAs, due to unknown reasons. Figure 1 gives the LVM spectra for samples treated in a hydrogen plasma. In all samples, we find two absorption lines, a stronger one around 780 cm^{-1} labeled X-$H1$ (X=S, Se, Te) and a weaker LVM, X-$H2$, around 1500 cm^{-1}. All of the LVM's show a weak frequency dependence on the donor mass. Table I gives a list of the exact spectral positions of the LVM's studied in this work. Substituting H by D shifts the spectral positions of lines as expected for hydrogen complexes. The ratio of the

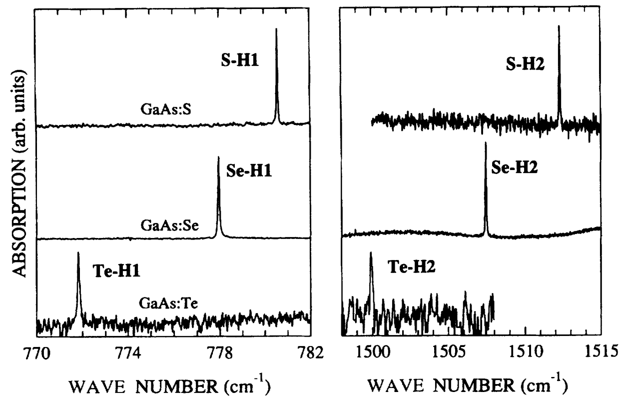

FIG. 1. Typical spectra of the stretching (right-hand side) and wagging modes (left-hand side) of the group-VI donor-hydrogen complexes in GaAs. Apodized resolution was 0.025 cm^{-1} for the X-$H1$ lines and 0.1 cm^{-1} for the X-$H2$ lines.

frequencies $r=\omega_{X\text{-}H}/\omega_{X\text{-}D}$ is almost $\sqrt{2}$ as predicted for an ideal harmonic oscillator. The precise r values are given in Table I.

The ratio of the integrated absorption of the lines X-$H1$ and X-$H2$ or X-$D1$ and X-$D2$ varies for the different donor species. The intensity ratio is, however, identical for the same complex in samples with different origin, thus manifesting that the origin of the two LVM's is due to the identical complex. All LVM's exhibit a strong temperature dependence. There is a drastic decrease in absorption and a frequency shift with increasing temperature.

Above 50 K no absorption of the X-$H2$ lines can be detected, whereas the X-$H1$ lines are still observable at 200 K. The LVM's show a drastic increase in linewidth and a shift towards lower frequencies with increasing temperature. At $T=6$ K, the lines are very sharp, all hydrogen lines have a full width at half maximum (FWHM) of below 0.1 cm^{-1} (see Table I). The corresponding deuterium LVM's show a drastical increase in linewidth by factors 5–10, similar to the case for the Si$_{\text{Ga}}$-H complexes.[6] We were not able to resolve any fine structure or asymmetry of the LVM's. Apparently, the asymmetry reported in Ref. 11 for the Se-H LVM was due to strain inhomogeneities.

TABLE I. List of LVM frequencies, full width at half maximum (FWHM) of the LVM's, relative intensities ($I_{X\text{-}H1}/I_{X\text{-}H2}$) and r values (with $r=\omega_{X\text{-}H}/\omega_{X\text{-}D}$).

Absorption line	Line position (10 K)	FWHM (10 K)	Relative intensity	r value (10 K)
S-$H1$	780.58 cm^{-1}	0.045 cm^{-1}	7.8	1.4035
S-$H2$	1512.30 cm^{-1}	0.071 cm^{-1}	1	1.3895
S-$D1$	556.1 cm^{-1}	0.3 cm^{-1}	7.6	
S-$D2$	1088.4 cm^{-1}	0.4 cm^{-1}	1	
Se-$H1$	777.95 cm^{-1}	0.08 cm^{-1}	7.3	1.4035
Se-$H2$	1507.46 cm^{-1}	0.08 cm^{-1}	1	1.3896
Se-$D1$	554.3 cm^{-1}	0.6 cm^{-1}	≈ 20	
Se-$D2$	1084.8 cm^{-1}	0.7 cm^{-1}	1	
Te-$H1$	771.81 cm^{-1}	0.09 cm^{-1}	5.5	
Te-$H2$	1499.93 cm^{-1}	0.13 cm^{-1}	1	

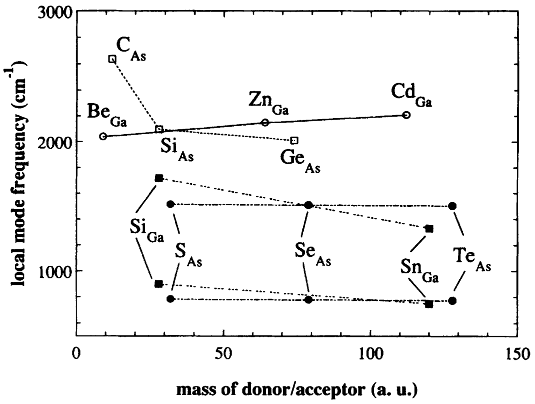

FIG. 2. Summary of all known acceptor- and donor-hydrogen mode frequencies in GaAs. References: C$_{\text{As}}$, Si$_{\text{As}}$, Ge$_{\text{As}}$, Be$_{\text{Ga}}$, Zn$_{\text{Ga}}$, Cd$_{\text{Ga}}$ (Ref. 8); Si$_{\text{Ga}}$, Sn$_{\text{Ga}}$ (Ref. 1); S$_{\text{As}}$, Se$_{\text{As}}$, Te$_{\text{As}}$, this work.

The LVM's detected in GaAs doped with chalcogens can be identified as the stretching mode at around 1500 cm^{-1} and the wagging mode at around 780 cm^{-1} of the chalcogen-hydrogen complexes. The characteristic frequency shift in the chalcogen-deuterium complexes gives unambiguous proof for the hydrogen incorporation. A ratio $r=\sqrt{2}$ indicates, however, that in the LVM's only the hydrogen atom is vibrating. All other constituents of the complex should have either large masses or strong force constants. The sample-independent intensity ratio of the two LVM's correlates those vibrations to the same complex. The intensity ratio, however, varies considerably for the different complexes and is clearly different from the ratio expected from the degeneracies of the vibrations (wagging mode:stretching mode = 2:1). From the frequencies (stretching mode $\approx 2\times$ wagging mode), the X-$H2$ or X-$D2$ LVM's could be interpreted as second harmonics of the X-$H1$ or X-$D1$ LVM's. However, in this case the ratio of absorption intensities should be much larger $[I(X\text{-}H1)/I(X\text{-}H2)\approx 1000]$ as was found for Zn-H complexes in GaAs.[15] Apparently, an assignment of hydrogen vibrational modes based on the relative intensities of LVM's is not reliable; this was already stated in Ref. 3.

In Fig. 2, we have summarized all available LVM frequencies of donor- and acceptor-hydrogen complexes in GaAs as a function of the donor or acceptor mass. The acceptor hydrogen complexes all have LVM frequencies above 1900 cm^{-1} and only a stretching mode was found for these complexes. Theory and experiment ask for a bond centered hydrogen position, and it is implied that the restoring forces for the displacement perpendicular to the axis between the hydrogen atom and the atom to which it is bound is very low, so that the mode occurs in the lattice continuum. The strong dependence of LVM's on the acceptor mass (C$_{\text{As}}$, Si$_{\text{As}}$, Ge$_{\text{As}}$) is explained by a direct bonding of hydrogen to the acceptors in the bond center position between acceptor and neighboring Ga atoms. There is only a weak mass dependence of the LVM's for the acceptors Be$_{\text{Ga}}$, Zn$_{\text{Ga}}$, and Cd$_{\text{Ga}}$. In these complexes, hydrogen is bound mainly to the neighboring As atom by reducing the bond strength to the acceptor. The LVM's are slightly modified As-H vibrations, the frequencies of which are well known from the stretching mode in arsine molecules. The local mode frequencies for the Si and Sn donor-hydrogen complexes are clearly smaller than those for the acceptor-hydrogen complexes. Two LVM's were found for each of these complexes. It was argued that wagging modes can only be detected when hydrogen is in an antibonding position. Elaborate studies determine the structure of these complexes as due to a direct binding of hydrogen to the donor atom, with hydrogen in the antibonding position.

The LVM's associated wth the chalcogen-hydrogen complexes show a behavior which is very similar to that of the corresponding complexes of the Si and Sn donors. The LVM frequencies are clearly reduced compared to the As-H stretching vibration. The appearance of stretching and wagging modes, similarities of the temperature dependence of line position and linewidth, and the increased linewidth for the deuterium complexes suggest a very similar complex. The only striking difference between the two groups of donors is the very weak dependence of the LVM frequency on the donor mass. However, this behavior is very similar to the donor-hydrogen complexes in Si. Only a small shift of 6 cm^{-1} occurs between the P-H and the Sb-H complexes. This behavior was explained by the binding of hydrogen to Si in the antibonding position opposite to the direction of the neighboring donor atom.

A very similar model was proposed for the group-VI donors in GaAs by Chang.[10] The independence from the donor mass is explained by the weak coupling of the donor to the hydrogen in the antibonding position at the neighboring Ga atom. The stretching frequency of these hydrogen complexes is basically the H-Ga stretching mode. In molecules, this frequency was determined to be at 1500 cm^{-1} (Ref. 16) in close agreement with our results.

There is however one open question which cannot be answered within the proposed model. Due to the natural abundance of Ga in the crystal, we would expect a splitting of all the stretching modes into two lines at an intensity ratio of 3:2. From our measurements no splitting or broadening could be correlated with the Ga isotopes. One could speculate about a strong binding of the Ga atom which is basically in an sp^2 configuration. Only under this assumption the Ga atom would not vibrate and not contribute to an isotope splitting.

In conclusion, by comparing the LVM's of three chalcogen-hydrogen complexes in GaAs we have found strong support for the defect model proposed by Chang. Hydrogen binds exclusively to Ga in the antibonding position without strong interaction with the neighboring chalcogen atom on the As site.

We would like to thank Panasonic Europe for the generous donation of the BOMEM FTIR spectrometer. The encouragement of H.J. Queisser and the technical assistance of H.-W. Krause are greatly appreciated. We are grateful to B. Pajot for providing us with a copy of his unpublished work on the same subject.

---

[1] S.J. Pearton, J.W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer, Berlin, 1992).

[2] *Hydrogen in Semiconductors*, edited by J.I. Pankove and N.M. Johnson (Academic Press, San Diego, 1991).

[3] M. Stavola, Mater. Sci. Forum, **148-149**, 251 (1994).

[4] S.J. Pearton, W.C. Dautremont-Smith, J. Chevallier, C.W. Tu, and K.D. Cummings, J. Appl. Phys. **59**, 2821 (1986).

[5] A.W.R. Leitch, Th. Prescha, and J. Weber, Phys. Rev. B **44**, 1375 (1991).

[6] B. Pajot, R.C. Newman, R. Murray, A. Jahil, J. Chevallier, and R. Azoulay, Phys. Rev. B **37**, 4188 (1988).

[7] B. Pajot, in *Shallow Impurities in Semiconductors*, Proceedings of the Third International Conference, Linköping, Sweden, 1988, edited by B. Monemar, IOP Conf. Proc. No. 95 (Institute of Physics, Bristol, 1989), p. 437.

[8] B. Pajot, B. Clerjaud, and J. Chevallier, in *Sixth Trieste Semiconductor Symposium on Hydrogen in Semiconductors, Trieste 1990*, edited by M. Stutzmann and J. Chevallier (North-Holland, Amsterdam, 1991), p. 371.

[9] D.M. Kozuch, M. Stavola, S.J. Pearton, C.R. Abernathy, and J. Lopata, in *Impurities, Defects and Diffusion in Semiconductors: Bulk and Layered Structures*, edited by D.J. Wolford, J. Bernholc, and E.E. Haller, MRS Symposia Proceedings No. 163 (Materials Research Society, Pittsburgh, 1990), p. 477.

[10] K.J. Chang, Solid State Commun. **78**, 273 (1991).

[11] J.H. Svensson and J. Weber, Mater. Sci. Forum **117-118**, 309 (1993).

[12] P.R. Briddon and R. Jones, in *Shallow Impurities in Semiconductors* (Ref. 7), p. 459.

[13] P.R. Briddon and R. Jones, Mater. Sci. Forum **65-66**, 169 (1991).

[14] P.R. Briddon and R. Jones, Phys. Rev. Lett. **64**, 2535 (1990).

[15] R. Darwich, B. Pajot, B. Rose, D. Robein, R. Rahbi, and B. Theys, *21st International Conference on the Physics of Semiconductors: Beijing, China, 1992*, edited by P. Chiang and H.-C. Cheng (World Scientific, Singapore, 1992).

[16] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV Constants of Diatomic Molecules* (Van Nostrand Reinhold Company, New York, 1979).