

Spectroscopy of hydrogen-related complexes in GaP:Zn

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Using infrared spectroscopy, local vibrational modes in GaP:Zn exposed to a remote hydrogen or deuterium plasma were observed. The modes at 2379.0 and 1729.4 cm^{-1} are assigned to hydrogen—phosphorus and deuterium—phosphorus bond-stretching modes of complexes adjacent to the zinc acceptors. The isotopic ratio $r = \nu_H / \nu_D = 1.3756$ is very close to that of the zinc-hydrogen complex in InP ($r = 1.3744$), which suggests that they have the same structure. © 1994 American Institute of Physics.

It is now well established that hydrogen passivates shallow impurities in III-V compound semiconductors.^{1,2} This was first observed by Johnson *et al.* who found that hydrogen passivates the zinc acceptor in GaAs.³ Although most studies have focused on GaAs and InP, significant work has been done on hydrogen passivation of impurities and defects in GaP. Singh *et al.* used photoluminescence spectroscopy to study hydrogen neutralization of donors, acceptors, and the isoelectronic nitrogen trap in GaP.⁴ Electrical measurements demonstrated that zinc in GaP is neutralized after exposure to atomic hydrogen.⁵ Clerjaud *et al.* observed the C—H and C—D bond-stretching local vibrational modes (LVMS)⁶ and the N—H mode⁷ in GaP grown by the liquid-encapsulation Czochralski (LEC) technique. LVMS corresponding to hydrogen-defect complexes in LEC-grown GaP have also been observed.^{8–11} Prior to this study, LVMS corresponding to a group-II acceptor-hydrogen complex in GaP have not been reported.

The GaP samples used for this study had a (100) orientation and were approximately 5 mm × 5 mm × 0.3 mm. Prior to zinc diffusion, they were *n* type, with $[S] \sim 10^{17} \text{ cm}^{-3}$. Following the procedure outlined by Chang *et al.*,¹² GaP samples were placed with 1 g zinc in an evacuated 180 ml quartz ampoule which had been cleaned in HF. The ampoule was placed in a vertical furnace and the GaP samples were diffused for 1 h at a temperature of 900 °C (Chang *et al.* observed the solubility of zinc in GaP at 900 °C to be $5 \times 10^{19} \text{ cm}^{-3}$). After completion of the diffusion, the samples were quenched to room temperature by dropping the ampoule into ethylene glycol. Residual zinc on the GaP surfaces was removed by immersion in dilute HCl. A room-temperature Hall-effect measurement with the van der Pauw geometry verified that the samples were *p* type after zinc diffusion. Some of the samples were then exposed to monatomic hydrogen or deuterium in a remote plasma system as described in Ref. 13. The hydrogenation temperature was 300 °C and the duration of the exposure was 3 h.

Infrared-absorption spectra were obtained with a Digilab 80-E vacuum Fourier-transform spectrometer with a KBr beamsplitter. Spectra were taken at 10 K with an instrumental resolution of 0.25 cm^{-1} . A Ge:Cu photoconductor was used as the detector. GaP:Zn samples which were not H- or D-plasma exposed were used as reference samples.

Spectra recorded with the hydrogenated and deuterated GaP:Zn samples show infrared-absorption peaks at 2379.0 and 1729.4 cm^{-1} , respectively, at 10 K (Fig. 1). The isotopic ratio of these frequencies, $r = \nu_H / \nu_D$, is 1.3756. Neither peak was seen in GaP:Zn which was not H- or D-plasma exposed. As a further check, we annealed a GaP sample for 1 h at a temperature of 900 °C in an evacuated quartz ampoule but with no zinc present. The sample was then exposed to a hydrogen plasma under the conditions described above. Again, neither peak was seen in the absorption spectrum. GaP:Zn samples which were exposed to a H/D plasma mixture showed both peaks but no new peaks which would have indicated a HD complex.

By way of comparison, hydrogenated InP:Zn has a bond-stretching mode at 2287.7 cm^{-1} and isotopic ratio $r = 1.3744$.¹⁴ The bond-stretching mode has been attributed to a H-P complex oriented along a bond-centered direction, adjacent to the Zn acceptor, with H essentially decoupled from Zn. Since the LVMS and the r factor for GaP:Zn are similar to the corresponding values for InP:Zn, we assume the structures are the same (Fig. 2). The H-P model receives further support from the observation that the LVM frequency

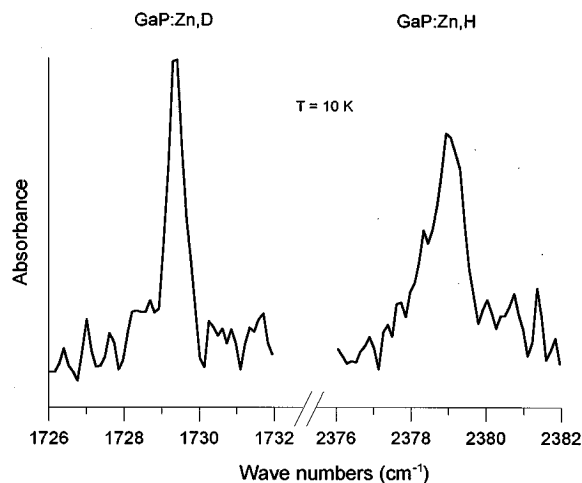


FIG. 1. Infrared-absorption spectra of deuterated and hydrogenated GaP:Zn. The vibrational modes are associated with H—P (D—P) complexes adjacent to the Zn acceptors.

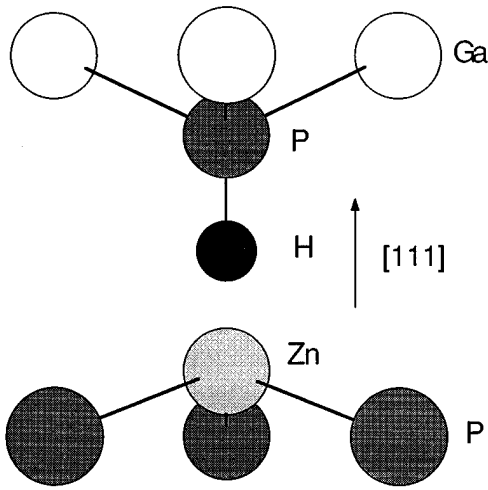


FIG. 2. Model for H passivation of the Zn acceptor with the H atom attached to a P atom in a bond-centered orientation.

is very different from the bond-stretching frequency of Zn–H (1600 cm^{-1}). This is in agreement with previous studies,^{15–18} which determined that in group-II acceptor-hydrogen complexes in GaAs, the hydrogen is bound directly to a neighboring arsenic atom.

It is known empirically that many X–H LVM frequencies are several percent lower in a crystal lattice than in a free molecule.¹⁹ The H–P LVMs in InP, for example, lie in the $2200\text{--}2300\text{ cm}^{-1}$ range, while the H–P bond-stretching mode of phosphine is 2328 cm^{-1} . An exception to this rule is the H–P mode in InP: Cd, which is found at 2332.4 cm^{-1} .²⁰ It now appears that the H–P mode in GaP: Zn is another exception, its frequency of 2379.0 cm^{-1} being approximately 2% higher than that of phosphine. The H–P mode in GaP: Zn is also higher than the H–P mode in InP: Zn; this may be related to the fact that GaP has a smaller lattice constant.

The positions and FWHM of the observed peaks are listed in Table I. The FWHM of the D–P peak at 10 K is approximately $2.2\times$ smaller than that of the H–P peak. This

TABLE I. Frequencies and FWHM of H–P and D–P LVM peaks in GaP: Zn and InP: Zn.

| Compound | H–P stretch mode | | D–P stretch mode | | $r = \nu_H/\nu_D$ |
|----------------------|------------------------------------|---------------------------|------------------------------------|---------------------------|-------------------|
| | Peak position (cm^{-1}) | FWHM (cm^{-1}) | Peak position (cm^{-1}) | FWHM (cm^{-1}) | |
| GaP: Zn | 2379.0 | 1.1 | 1729.4 | 0.5 | 1.3756 |
| InP: Zn ^a | 2287.7 | 0.23 | 1664.5 | 0.08 | 1.3744 |

^aSee Ref. 1.

effect has been observed in numerous hydrogen-related complexes in III–V semiconductors and is related to the smaller average vibrational amplitude of the D atom as compared to the H atom. In InP: Zn, for example, the D–P peak at 6 K is narrower than the H–P peak by a factor of 2.9.

In conclusion, by using infrared-absorption, we have discovered vibrational modes in GaP: Zn exposed to H and D plasma. The similarity between these modes and the H–P and D–P modes in InP: Zn suggests that they also correspond to H–P and D–P bond-stretching modes oriented along a bond-centered direction.

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