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Local Vibrational Mode Spectroscopy of Beryllium- and Zinc-Hydrogen Complexes in GaP

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Abstract. Using infrared absorption spectroscopy, we have observed local vibrational modes in GaP:Be and GaP:Zn exposed to a remote hydrogen or deuterium plasma. In GaP:Zn, we attribute the modes at 2379.0 cm^{-1} and 1729.4 cm^{-1} to hydrogen-phosphorus and deuterium-phosphorus bond-stretching modes of complexes adjacent to the zinc acceptors. In GaP:Be, we attribute the modes at 2292.2 cm^{-1} and 1669.8 cm^{-1} to similar complexes adjacent to the beryllium acceptors.

1. Introduction

The subject of hydrogen passivation of defects and impurities in compound semiconductors has attracted a great deal of interest in recent years. Although most studies have focused on GaAs and InP [1,2], significant work has been done on hydrogen passivation in GaP. Singh *et al.* used photoluminescence (PL) spectroscopy to study hydrogen neutralization of donors, acceptors, and the isoelectronic nitrogen trap in GaP [3]. Electrical measurements demonstrated that zinc in GaP is neutralized after exposure to atomic hydrogen [4]. Clerjaud *et al.* observed the C-H and C-D bond-stretching local vibrational modes (LVM's) [5] and the N-H mode [6] in GaP grown by the liquid-encapsulation Czochralski (LEC) technique. LVM's corresponding to hydrogen-defect complexes in LEC-grown GaP have also been observed [7]. Prior to this study, LVM's corresponding to group II acceptor-hydrogen complexes in GaP have not been reported.

2. Experiment

The GaP samples used for this study had a (100) orientation and were approximately 5 mm X 5 mm X 0.3 mm. Prior to zinc diffusion, they were n-type, with a sulfur concentration of around 10^{17} cm^{-3}. To obtain GaP:Zn, 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 hr at a temperature of 900°C. 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. 8. The hydrogenation temperature was 300°C and the duration of the exposure was 3 hr.

To obtain GaP:Be, GaP samples were implanted with Be ions at energies of 40 keV, 100 keV, and 200 keV, for a total dose of 2.5 X 10^{15} cm^{-2}, followed by a rapid thermal anneal at 1000°C for 10 s. A room temperature Hall effect measurement indicated a hole concentration of 2.5 X 10^{15} cm^{-2} prior to hydrogenation.

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 and GaP:Be samples which were not H- or D-plasma exposed were used as reference samples.

3. Results

Spectra recorded with the hydrogenated and deuterated GaP:Zn samples show infrared absorption peaks at 2379.0 cm^{-1} and 1729.4 cm^{-1}, respectively, at a temperature of 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 hr 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. Free carrier absorption prevented measurements below 1300 cm^{-1}.

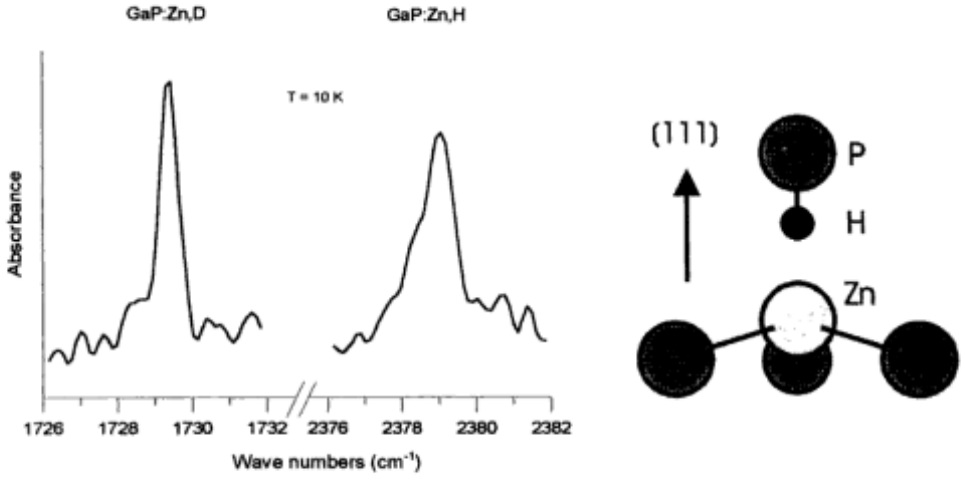

Figure 1. Infrared absorption spectra of deuterated and hydrogenated GaP:Zn and suggested model for H-passivation.

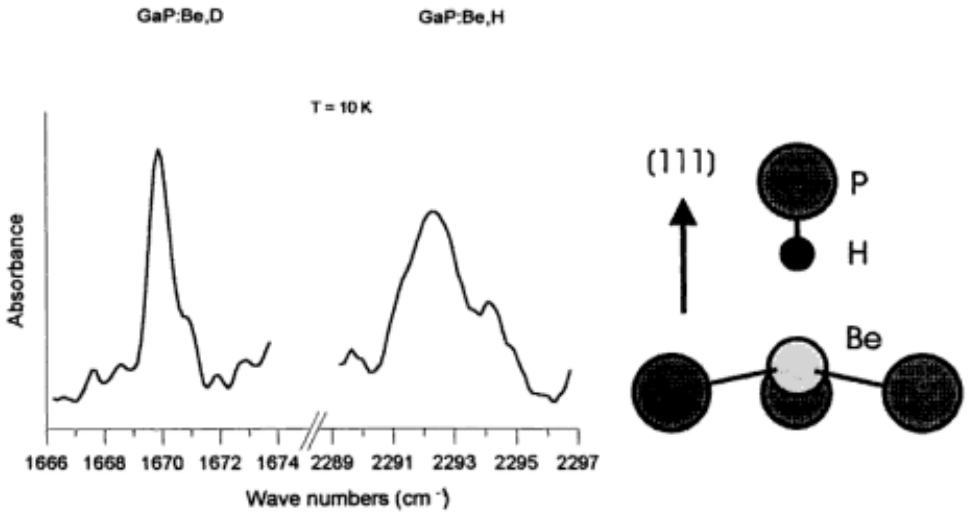

Figure 2. Infrared absorption spectra of deuterated and hydrogenated GaP:Be and suggested model for H-passivation.

By way of comparison, hydrogenated InP:Zn has a bond-stretching mode at 2287.7 cm^{-1} and isotopic ratio r = 1.3744 [9]. 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 LVM's and the r-factor for GaP:Zn are similar to the corresponding values for InP:Zn, we assume the structures are the same. The H-P model receives further support from the observation that the LVM frequency is very different from the bond-stretching frequency of Zn-H (1600 cm^{-1}). This is in agreement with pervious studies [10], which determined that in group II acceptor-hydrogen complexes in GaAs, the hydrogen is bound directly to a neighboring arsenic atom.

The hydrogenated and deuterated GaP:Be samples show infrared absorption peaks at 2292.2 cm^{-1} and 1669.8 cm^{-1}, respectively, at a temperature of 10 K (Fig. 2). The isotopic ratio of these frequencies, $r = \nu_H/\nu_D$, is 1.3727. Neither peak was seen in GaP:Be which was not H- or D-plasma exposed. Once again, these values are similar to the corresponding values in hydrogenated InP:Be, which has a H-P bond-stretching mode at 2236.5 cm^{-1} and isotopic ratio r = 1.3714. We therefore assume that the absorption peaks arise from a H-P complex oriented in a bond-centered direction, adjacent to the Be acceptor.

The H-P modes in GaP are higher than the H-P modes in InP; this may be related to the fact that GaP has a smaller lattice constant. In addition, the H-P modes in GaP:Zn are higher than the H-P modes in GaP:Be. The increase in hydrogen bond-stretching frequencies with increasing group II acceptor size has also been observed in InP and GaAs.

The positions and FWHM of the observed peaks are listed in Table I. The FWHM of the D-P peaks at 10 K are approximately twice as small as those of the H-P peaks. This 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.

Compound	H-P stretch mode		D-P stretch mode		$r=\nu_H/\nu_D$
	Peak (cm^{-1})	FWHM (cm^{-1})	Peak (cm^{-1})	FWHM (cm^{-1})	
GaP:Be	2292.2	1.8	1669.8	0.7	1.3727
InP:Be[a]	2236.5	0.43	1630.9	0.2	1.3714
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

[a]Ref 1.

Table 1. Frequencies and FWHM of hydrogen LVM peaks in GaP and InP.

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