Evidence for Complexes of Hydrogen with Deep-Level Defects in Bulk III-V Materials

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Series of sharp optical-absorption lines around 2000 cm^{-1} in GaAs, 2300 cm^{-1} in InP, and 2200 cm^{-1} in GaP are reported. They are shown to be due to the vibration of As—H or P—H bonds, the hydrogen sitting near a transition-metal impurity or other defect. The "chemical shift" of the line is characteristic of the impurity or defect. A model of these centers is proposed.

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The passivation of shallow acceptors or shallow donors in the semiconductors Si[1,2] or GaAs[3-6] by hydrogen is an active subject of investigation. Recently, the neutralization of deep electron traps in molecular-beam epitaxial (MBE) GaAs layers has also been reported.[7,8] All these works had been performed with materials intentionally doped with hydrogen either by diffusion of molecular or atomic hydrogen or by crystal growth under hydrogen atmosphere.

In the present Letter we report on a spectroscopical study which shows that hydrogen is present in nonintentionally hydrogen-doped III-V bulk materials and that it forms complexes with transition-metal impurities and other deep-level defects. The analysis of the spectroscopical data allows us to determine the structure of these complexes.

We performed infrared absorption experiments by Fourier-transform spectroscopy using a Michelson interferometer (Bomem DA3.01) equipped with a globar source, a KBr beam splitter, and a cooled mercury cadmium telluride detector. The samples were cooled in a continuous-flow helium cryostat (Oxford Instruments CF 204) allowing experiments at temperatures between 5 K and room temperature.

The GaAs and GaP materials studied were all grown by the liquid-encapsulated Czochralski (LEC) technique. One of the GaAs samples studied was a polycrystal. The InP samples were either LEC-grown materials or small single crystals coming from polycrystalline ingots issuing from the InP synthesis. All the samples studied were doped with transition-metal impurities; none of them was intentionally doped with hydrogen.

In indium phosphide, we observed[9] five different very sharp absorption lines (linewidth <0.1 cm^{-1} at liquid-helium temperature) in a narrow energy range around 2300 cm^{-1}. They are listed in Table I. The observation of four of them is clearly correlated with the dopants present in the crystal: The lines are only seen in the samples in which the impurities are present and they are observed in all the samples having this characteristic doping whatever is the origin of the sample. However, the intensity of the line is not correlated with the concentration of dopant. The last one at 2315 cm^{-1} is very frequently observed and should be related with either a lattice defect or a common contaminant of the InP material.

In gallium arsenide we observed six lines (cf. Table I) of the same width as in InP but at lower energy than in InP: approximately between 2000 and 2050 cm^{-1}. Most of them are observed with various dopants and therefore cannot be related with a specific impurity except the line at 2009.5 cm^{-1} at 5 K which has only been observed in iron-doped samples. A typical spectrum evidencing three of these lines is shown in Fig. 1.

In gallium phosphide samples one sharp line at 2204.3 cm^{-1} at 5 K has been detected in several samples.

In the spectral region considered, sharp lines can have two different origins: They can be either zero-phonon lines of electronic transitions or vibrational transitions. The behavior of the lines when the temperature is changed enables us to discriminate between these two possibilities: The electronic zero-phonon lines broaden and rapidly disappear when the temperature is increased, whereas the vibrational transitions are very weakly affected by temperature variations. The experiments

TABLE I. Energies of the transitions observed at 5 K in various III-V compounds and tentative assignments to defects.

Compounds	Energy (cm^{-1})	Impurity or defect involved
GaP	2204.3	
GaAs	2001.0	
	2009.5	Fe
	2011.4	
	2020.6	
	2024.3	
	2051.8	
InP	2272.0	Mn
	2285.7	V (n-type samples)
	2287.7	V (p-type samples)
	2300.0	Ti
	2315.6	

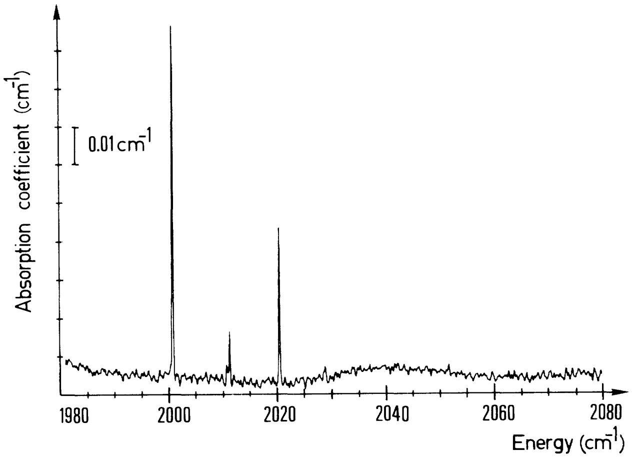

FIG. 1. Absorption spectrum of a GaAs sample showing three of the lines quoted in Table I.

show that the lines stay quite sharp when the temperature is increased: Their linewidth is still smaller than 0.5 cm^{-1} at 200 K. This indicates the vibrational nature of the transitions. A slight energy shift towards low energies is observed when the temperature increases; this energy shift is of the order of 1.5 cm^{-1} when the temperature increases from 5 up to 200 K. The vibrational nature of the transitions we observe is confirmed by the fact that we have not been able to detect any luminescence corresponding to the sharp absorption lines.

As the energy of these vibrational lines is very high, they must involve very light species; in fact, hydrogen is the only possible candidate. Table II summarizes the energies of the absorption bands of the stretching modes of vibration of the As—H and P—H bonds observed in proton-implanted or amorphous hydrogenated GaAs, GaP, and InP materials. It is to be noted that the width of these bands is larger than the sharp-line ones reported in the present Letter by about three orders of magnitude.

Comparison of Tables I and II shows that in the three materials the energies of the lines presently reported are in the same range as those of the stretching modes of the As—H and P—H bonds. This is good proof that we are dealing with stretching vibrations of As—H and P—H bonds.

TABLE II. Energies of the stretching As-H and P-H vibrational modes in GaP:H, GaAs:H, and InP:H.

Compound	Energy (cm^{-1})	Type of material	Reference
GaP	2204	Proton implanted	10
	2220	Amorphous hydrogenated	11
GaAs	1998	Proton implanted	12
	2040	Amorphous hydrogenated	11
InP	2197 2212	Proton implanted	13

Most transition-metal impurities at metallic sites act as deep acceptors in III-V materials.[14,15] This is also the case for several defects. In pure III-V materials, each group-III atom provides three electrons to its four bonds. If a group-III atom is replaced by a substitutional transition metal or other defect which provides only two electrons, then one of the four ligands (arsenic or phosphorus), having an unpaired electron, will be unsatisfied; hydrogen can bind to this ligand and supply the pairing electron. This model, analogous to the model of neutralization of substitutional boron in silicon,[1] is schematized in Fig. 2; in the case of boron in silicon, theoretical investigations[16] have confirmed it. In this model, the transition-metal impurity or defect affects the "length" of the As—H or P—H bond and therefore its spring constant; this induces a "chemical shift" of the vibrational energy. Therefore, the model explains the series of lines observed in each compound depending on the transition-metal dopant or defect. It also explains the slight shift towards low energies when the temperature increases: The thermal expansion of the lattice increases the bond "length" and therefore weakens the bond, shifting the vibrational absorption line towards low energies.

In indium phosphide, where four of the observed lines are clearly associated with titanium, vanadium, and manganese, one observes that the vibrational energy decreases from titanium to manganese. This can be understood in the frame of the proposed model: The radii of the atoms decrease from titanium to manganese, which means that the nearby hydrogen-phosphorus bond "length" will increase from titanium to manganese, and therefore that the vibrational energy will decrease from titanium to manganese as observed experimentally.

An important question is whether these centers are

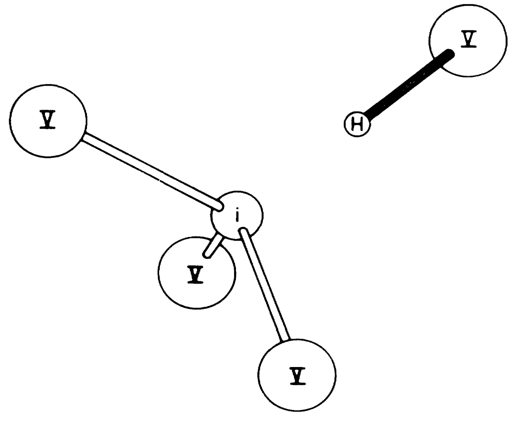

FIG. 2. Schematic structures of the centers viewed along a ⟨100⟩ direction. The absorption lines observed are due to stretching vibrations of the shaded bond. H, i, and V denote hydrogen, impurity (or defect), and group-V atoms, respectively.

electrically active or not. The model is, in fact, a scheme of neutralization (or passivation) of the acceptor and therefore one does not expect electrical activity for these complexes. This type of center is probably responsible for the neutralization of deep electron traps observed in MBE GaAs materials[7,8] and the proposed model can also be applied to the passivation of shallow acceptors in GaAs.[3] However, in the case of vanadium in InP, two clearly distinct lines have been observed depending on whether the samples are *n* type or *p* type. Vanadium in InP has been shown to act as a deep donor[17,18] whose energy level is 0.21 eV above the valence-band maximum[17,18]; however, the "acceptor" level has been predicted to be in the conduction band but very close to its minimum.[19] We believe that the acceptor level of the V-H complex is lower than the "acceptor" level of "isolated" vanadium, as has been shown to be the case for the copper-hydrogen complexes in germanium,[20] and therefore that the acceptor level of the V-H complex lies within the band gap. Therefore, we assign the 2285.7-cm^{-1} line to the negatively charged $(\mathrm{V\text{-}H})^-$ complex and the 2287.7-cm^{-1} line to the neutral $(\mathrm{V\text{-}H})^0$ one. The lower energy of the negatively charged complex can also be explained by the model: The negatively charged complex will have a tendency to repel the phosphorus ligands allowing a longer bond "length" for the negatively charged complex than for the neutral one, and therefore a lower energy of vibration for the negatively charged complex than for the neutral one.

This work is to be related to the copper-hydrogen complexes observed in germanium[20,21] by photothermal ionization spectroscopy; it is quite possible that the model proposed in this Letter could also apply to the copper-hydrogen complexes in germanium. Copper, being a triple acceptor in germanium, can form complexes with one, two, or three hydrogens[20]; every binding could be of the type reported in this Letter. In this respect it is of interest to look to the vibrations of Ge—H bonds in Ge:Cu,H.

The source of hydrogen pollution of the materials is not clear: It can come either from the starting material or from the cap, made from wet boric oxide, used during the LEC growth. In the case of InP some contamination could also come from the quartz used during the synthesis. At present we are not able to specify the concentration of the centers, because of the lack of cross section of the observed transitions.

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