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HYDROGEN IN InP–BONDING AND PASSIVATION*

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A tight-binding total energy calculation shows that the possible hydrogen-indium bond in InP is long and weak whereas hydrogen–phosphorus bond is short and strong. The model explains the known experimental data, especially the lack of local vibrational modes of InH in InP implanted with protons and hydrogen passivation of acceptors but not donors in InP.

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Recently, hydrogenation of defects and impurities in elementary and compound semiconductors has arisen general interest (see reviews [1] and [2]). However, although these phenomena happen also in InP (see proceedings [3]), acceptors in this material are passivated more easily than donors. This asymmetry of passivation corresponds to no InH local vibrational modes observed in indium phosphide after proton implantation — only PH molecular bonds were detected in InP bombarded with hydrogen ions or in as-grown crystals. The latter contamination is probably due to hydrogen from wet B_2O_3 encapsulant used during growth.

In this paper we show that simple bonding and topological arguments can explain the peculiar properties of hydrogen in InP.

The tight-binding total energy calculational method is essentially the same as in our previous paper [4]. First we consider the total energy of a vacancy in InP saturated with a single hydrogen. For III–V compounds, we have two different vacancies: missing indium or missing phosphorus atoms in the perfect lattice. For indium vacancy the phosphorus dangling hybrid of the sp^3 character can be saturated by hydrogen. The calculated bond length is short ($d = 1.42$ Å) and
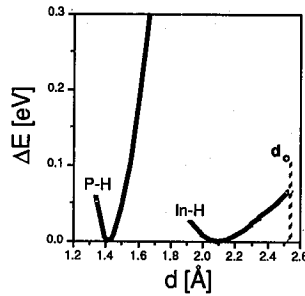

Fig. 1. Changes of the energy of hydrogen atom bonded with phosphorus or indium lattice ions in InP as the function of the bond length (see also text).

tunneling of the hydrogen atom is not possible between four dangling hybrids of four phosphorus atoms in the unit cell. For phosphorus vacancy the indium dangling hybrid can also be saturated by hydrogen. Assuming the indium hybrid is of sp^3 type, one gets the InH bond length of 2.06 Å. This is about 0.26 Å longer than reported for InH molecule [5]. However, for linear molecule one is probably dealing not with sp^3 but with sp hybrid. The calculated InH bond length for sp hybridization is 1.87 Å, agreeing with the experimental value of 1.83 Å [5]. In the Table we present the calculated bond lengths for $sp^3 - s$ and $sp - s$ hybridizations of the cation hydrides for III–V compounds and the experimental bond lengths [5] observed for molecules in the gaseous phase. One can easily see that the values agree well for the studied systems. This leads us to the conclusion that the lack of InH bonds in InP is resulting from their extreme length.
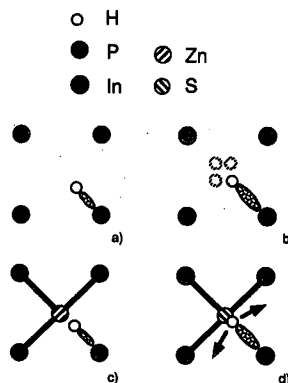

Fig. 2. Possible hydrogen configurations for different defects in InP lattice: (a) indium vacancy; (b) phosphorus vacancy; (c) zinc acceptor; (d) sulphur donor.

TABLE

Bond lengths for group III hydrides.

Molecule	d_{sp^3-s}[Å]	d_{sp-s} [Å]	d_{exp}[Å]
B-H	1.20	1.15	1.23
Al-H	1.68	1.57	1.65
Ga-H	1.76	1.62	1.66
In-H	2.09	1.87	1.83

In Fig. 1 we show the comparison between the calculated potential energies versus bond length for indium and phosphorus vacancies saturated with hydrogen (sp^3 models). We note that the bond length of InP lattice is $d_o = 2.52$ Å. The curvature of the energy-distance plot is flat for InH bond, suggesting tunneling between next sites (á la floating bonds — see Fig. 2b, where broken lines show the three other possible sites).

Now let's discuss hydrogen passivation of impurity centers. In Fig. 2c we show that for acceptors (like zinc) in InP the fourth, free dangling bond in the defect can be easily saturated with hydrogen since it belongs to the phosphorus atom and forms sp^3 dangling hybrid. For donors (like sulphur) the situation is more complex. The added, fifth charge has to be fitted somewhere inside the defect. Working in the frame of our model we've calculated that part of this charge is at sulphur ion, repulsing away the hydrogen atom from the long indium–hydride bond, see Fig. 2d. One should also consider the so called back-bonding position of hydrogen for this defect (see our previous paper [5]). However, the indium-hydrogen bond becomes here $p-s$ like. The $p-s$ bond length is even longer ($d = 2.34$ Å) than the sp^3-s one. This may prevent the hydrogen from moving to the next lattice cell because of the repulsion by the neighbor phosphorus atom.

The described mechanism of hydrogen bonding in InP explains the observed experimental data without invoking unclear hydrogen electronic levels in the gap [6]. Moreover, we believe that our simple model provides a good starting point for making more rigorous first-principle calculations.

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