

H-induced passivation of GaAs(110)-Be surface-acceptor systems

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Complete neglect of differential overlap cluster calculations have been performed for H^+ on a clean GaAs(110) surface. The results demonstrate that H^+ prefers to bond with the surface As atom rather than the surface Ga atom. Investigation of a microscopic model for hydrogen (H)-induced passivation on p -type GaAs(110) surfaces, where a surface Ga atom is replaced by a Be acceptor atom, also shows that, in equilibrium, the H atom attaches itself to the dangling bond of the As atom next to the Be atom. Passivation occurs due to compensation when the H atom captures a free hole to form H^+ which then subsequently finds the As atom next to the acceptor. This microscopic model may account for the As-H stretching lines observed in infrared experiments as well as for the absence of Ga-H lines.

I. INTRODUCTION

The discovery that hydrogen (H) is able to bond to and passivate the electrical activity of dangling or defective bonds in semiconductors^{1,2} has led to increased activity in research involving experimental and theoretical studies of the properties of H in semiconductors.³ By itself, the mobile atomic hydrogen diffuses rapidly^{4,5} and forms complexes with crystal defects and impurities.⁶⁻¹¹ However, most of the available data on H-induced passivation in semiconductors tend to focus on its properties in the bulk of semiconductors, especially Si, with well-established models of the H-dopant complexes and passivation mechanism. Acceptors can be passivated by H in Si, GaAs, Ge, and InP while donor passivation is observed in Si, GaAs, and $Al_xGa_{1-x}As$, although for Si, the situation is not so clear, with only one report of partial passivation of P-doped n -type Si.⁸ H passivation of p -type semiconductors is attributed to the direct compensation between free holes and H resulting in H^+ which then pairs up with the acceptor impurity A^- to form an inactive H-acceptor complex $[(HA)^0]$. Thus H-acceptor pairing is a consequence, not the cause of passivation, with H having a deep donor level in the gap.^{12,13} The passivation model above with H having a donor level can then account for the evident lopsidedness in the experimental data for Si: H passivates p -type Si thoroughly, but has either no effect^{1,2} or partial effect⁸ in n -type Si.

In contrast, there is still a scarcity of data, theoretical and experimental, regarding the interaction of H with impurities on the semiconductor surfaces, especially for the III-V compounds.¹⁴ The passivation mechanism at the surface is not yet fully understood, unlike the case for the bulk for III-V compounds. In the bulk, work has been performed on the neutral H in III-V compounds.¹⁵⁻¹⁷ In GaAs, H appears to bond to a substitutional As atom, occupying the antibonding (AB) site next to the As atom¹⁵ although Maric *et al.*¹⁶ only investigated the bond-centered site for the H atom. In our work on H in GaP,¹⁷ we also find that H prefers to bond with a substitutional P atom, i.e., in Ga-V compounds, the isolated neutral H prefers bonding with the group-V atom. From

calculations of H on clean GaAs(110) surfaces¹⁸ and surface sensitive spectroscopy experiments [electron-energy-loss spectroscopy (EELS) and ultraviolet photoemission spectroscopy (UPS)] on chemisorption of H on GaAs(110),¹⁹ H atoms chemisorb at the early stages along the dangling bond directions of the ideal not relaxed surface, removing the surface reconstruction. Thus H favors bonding with the usual chemisorption sites, namely, saturating the dangling bonds of the surface Ga and As atoms. In the bulk for p -type GaAs, the bond-centered model appears to apply,^{20,21} with H between the Si_{As} acceptor and a Ga atom²⁰ in one model while the other has H near the center of a Be_{Ga} -As bond.²¹

On the other hand, to the best of our knowledge, only one model has been proposed for H-induced passivation of acceptors (e.g., Zn or Be) on the GaAs surface which so far has never been theoretically verified.²² This model has the H atoms attached to the dangling bonds of As atoms close to Zn_{Ga} or Be_{Ga} ,²² concluded from infrared (IR) measurements where strong As-H stretching lines have been observed while Ga-H lines are absent, for which no reason is known.^{22,23} InP is also found to exhibit a similar behavior.^{24,25} Interestingly, the diffusion characteristics of deuterium in p -type GaAs and InP suggest that in these materials, hydrogen diffuses as positively charged species²⁶ and the motion of H^+ has been observed in p -type GaAs (Ref. 27) recently. Thus, for p -type GaAs surfaces, H^+ is expected to be present too. While there has been some work on the clean GaAs(110) surface,^{18,19} both theoretically and experimentally, detailed theoretical work on the interaction of H with dopants on the GaAs(110) surface is still lacking although Manghi *et al.*²⁸ did perform self-consistent pseudopotential calculations for H deposited on the unrelaxed GaAs(110) surface, with H chemisorbed on both Ga and As sites. They showed that H adsorption gives rise to strong modifications in the whole valence spectrum.

In this paper we present one of the first theoretical calculations of a microscopic model for a H-acceptor (Be) system on the GaAs(110) surface to account for the presence of the As-H stretching lines observed from IR experiments at the expense of the Ga-H lines.^{22,23} We attri-

TABLE I. The CNDO parameters used.

Atom	Electronegativity (eV)		Bonding parameter (eV)	Orbital exponent (bohr ⁻¹)
	ϵ_s	ϵ_p		
Ga	7.10	4.05	-2.2	1.802
As	8.00	4.00	-9.9	1.920

bute this to the passivation mechanism as discussed above with H having a donor level leading to the production of H^+ after initial compensation, as observed experimentally. Due to the dependence of the equilibrium configuration of H on the GaAs(110) surface on its charge state, H^+ prefers to reside on an As site rather than a Ga site, thus accounting for the As-H lines observed from IR experiments. Hence our results provide theoretical support to the proposed model²² above where by the H atoms are attached to the dangling bonds of As atoms close to Zn_{Ga} or Be_{Ga} .

II. THEORETICAL METHOD

Since, in our work here, we are interested in determining the equilibrium configuration of a H atom on the GaAs(110) surface with a Be (acceptor) atom replacing a surface Ga atom, the method we employ must be able to give the total energy of the defect system, that is, it incorporates a total-energy algorithm. We use the complete neglect of differential overlap (CNDO) method²⁹ in which the matrix elements of the Hartree-Fock-Roothaan equations are systematically approximated via the introduction of three semiempirical parameters: an orbital exponent, the electronegativities, and a bonding parameter. These approximations then yield self-consistent solutions analogous to Hartree-Fock solutions. We implement the MOSES code³⁰ with the H and Be parameters from Pople and Beveridge²⁹ whereas the GaAs parameters (see Table I) are those Chia and Ong have recently determined³¹ by fitting the calculated bulk properties to the experimental values of the cohesive energy, the lattice constant, and the valence bandwidth using a 16-atom periodic large unit cell of GaAs. This method has been used successfully to investigate H in Si,⁴ Ge,⁵ and GaP,¹⁷ the Bourgoin-Corbett mechanism of self-interstitials in Si (Refs. 32 and 33) and Ge (Ref. 34) as well as H-induced passivation in doped Si.^{9,11} In addition, it has recently been applied to investigate desorption induced by electronic transition (DIET) processes on semiconductor surfaces.³⁵⁻³⁷

III. CLUSTER DESCRIPTION AND CALCULATIONS

An 84-atom surface cluster is used to simulate the GaAs(110) surface. This cluster has been used previously to study the desorption of Ga and P atoms from defect sites on the GaP(110) surface.³⁵⁻³⁷ The dangling bonds at the edges of the cluster are saturated by hybrid pseudoatoms of Ga and As whose parameters reflect their relative charges of 0.75 and 1.25. There are at least four shells of nearest-neighbor bulk atoms around the central surface atoms to minimize any edge effects. Further details regarding the surface cluster have already been

presented in Refs. 35-37. Supplementary calculations are also performed on bulk clusters^{4,5,9,11,17} comprising 70 atoms for H at major interstitial sites (*T*, *H*, and *AB*) in bulk GaAs as an initial test to compare with other calculations.^{15,16} For the isolated H, it prefers an antibonding interstitial site, 1.58 Å away from a substitutional As atom, consistent with the results of Pavesi and Giannozzi.¹⁵

For H on GaAs(110), we perform our calculations on an ideal GaAs(110) surface, an assumption which is not unrealistic based on experimental and theoretical evidence that chemisorption of H takes place on chemisorption sites of the unrelaxed substrate through covalent direction bonds,^{14,18,19,28} i.e., H saturates the dangling bonds of the surface atoms. Figure 1(a) illustrates the top view of the ideal GaAs(110) surface while Fig. 1(b) shows the situation when a surface Ga atom is replaced by a Be (acceptor) atom. We place the H atom at three adatom sites labeled (i) above the Be site, (ii) above the As site, nearest neighbor to the Be atom, and (iii) above the Ga site next to the As atom in (ii). For each configuration, the H atom is moved along the $\langle 111 \rangle$ dangling bond

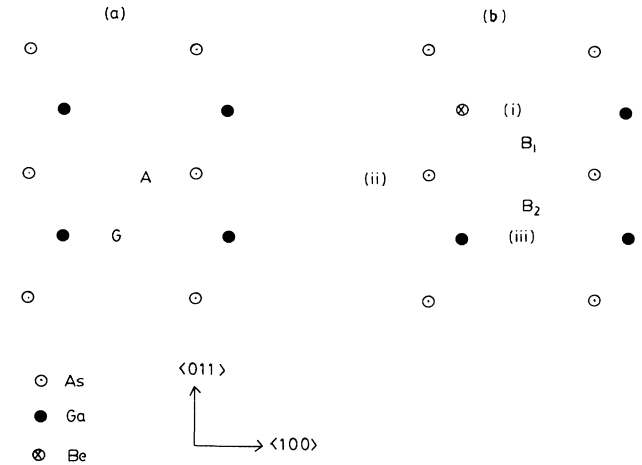


FIG. 1. (a) Top view of a clean GaAs(110) surface. For each case, the isolated K and H adatoms in the positive and neutral charge states are attached to the dangling bonds of the surface As and Ga surface atoms (As site and Ga site), labeled *A* and *G*, respectively. The findings are discussed in the text. (b) Top view of a *p*-type GaAs(110) surface, GaAs(110):H-Be system. The total energies of the H atom at sites (i)–(iii) and at bridge sites *B*₁ and *B*₂ are calculated and the results are illustrated in Table II. In the presence of the acceptor (Be) atom on GaAs(110), the H atom prefers to attach itself to the dangling bond of the As atom next to the acceptor atom. Bridge sites *B*₁ and *B*₂ are higher in energy, suggesting that H prefers the dangling-bond sites.

direction of the surface atom as well as along the $\langle 110 \rangle$ direction, perpendicular to the surface to determine the minimum energy configuration for each site. The values of the final total energies of the three sites are then compared to yield the global minimum with respect to the surface sites investigated. Supplementary calculations whereby the H atom is placed at the bridge site between the Be atom and As atom on a neighboring zigzag chain (site B_1) and the adjacent bridge site between the Ga nearest neighbor of the Be atom on the same zigzag chain and an As atom (site B_2) are also carried out to compare the preference of the H atom to dangling bond sites [see Fig. 1(b)].

IV. RESULTS AND DISCUSSIONS

Klepeis and Harrison³⁸ have used the tight-binding formalism to investigate the bonding sites for individual monovalent and trivalent metal atoms in different charge states (positively charged and neutral) on GaAs(110) and found that the neutral adatoms prefer to bond to a surface Ga atom while the positively charged adatoms favor the As sites (bonding with surface As atoms). Motivated by their findings for metal adatoms, we first repeat their calculations for K and K^+ adatoms on GaAs(110) and obtain the same results, that is, the neutral K adatom prefers the Ga (G) site while the K^+ adatom prefers the As (A) site [see Fig. 1(a)]. We also extend the calculations to include H and H^+ adatoms on GaAs(110), of relevant interest to our investigation of H-acceptor systems on GaAs(110). Our results show that both the isolated H and H^+ adatoms prefer the As site over the Ga site, with the H^+ adatom at the As site lower in energy than that at the Ga site by about 1.6 eV while the neutral H adatom shows a weaker preference by 0.4 eV. For the neutral case, when the surface atom to which the H atom is attached is relaxed, the total energy reduces slightly but the preference for the As site is still maintained, with the As site lower by about 0.33 eV. On the experimental side, core photoemission studies of H chemisorption on GaAs(100) and GaAs(111) polar surfaces by Bringans and Bachrach³⁹ suggest that H is mainly bonded to As atoms on both surfaces. Moreover, UPS studies⁴⁰ of the H-GaAs(110) system in the low-coverage regime, for which our simulation applies since we are investigating isolated H and H^+ adatoms, also favor H-As bonding. This could be due to the relative stability of the H-As bond compared to the Ga-H bond (Ga hydride molecules are unstable⁴¹). Thus our findings for the equilibrium configurations of both the isolated H and H^+ adatoms on GaAs(110) appear to be consistent with experimental results although the smaller barrier for the neutral H adatom case at the As site relative to the Ga site does not preclude the possibility of direct bonding of atomic H to Ga and As surface atoms in the high-coverage regime as observed experimentally.⁴²

With regards to the phenomena of H passivation of p -type GaAs surfaces, the mechanism which leads to passivation is not yet fully understood.¹⁴ But, if we were to extend the argument derived from the bulk with H having a donor level^{12,13} for p -type semiconductors, then the

TABLE II. Calculated results for various configurations of a GaAs(110):H-Be system. The zero of the energy is at the global minimum site.

	Be site	Ga site	As site
Total energy of H atom (in eV) at	0.95	1.98	0.00
H- X bond length (\AA) ($X = \text{Be, Ga, or As}$)	1.78	1.69	1.65

initial compensation should lead to the formation of H^+ on the surface, which, for the case of GaAs(110), preferentially favors bonding with the surface As atom rather than the surface Ga atom as calculated above. Such a model may then account for the strong As-H stretching lines, at the expense of Ga-H lines which are absent, as observed from infrared experiments.^{22,23}

To confirm this model, total-energy calculations are carried out on a model representing a H-acceptor system on a III-V (110) surface, that is, a H-Be acceptor system on GaAs(110) surface [see Fig. 1(b)] as described in Sec. III, with the H atom placed at five different sites, (i) above the Be atom, (ii) the As atom, (iii) the Ga atom next to the As atom in (ii), along their dangling bond directions, and the bridge sites between (iv) Be and As (site B_1), and (v) Ga and As (site B_2). Our calculations yield the results illustrated in Table II for the dangling bond sites. As can be seen, H attached to the surface As atom [site (ii)] next to the Be atom occupying a surface Ga site has the lowest energy, being about 0.95 eV below that for the Be site [site (i)] and 2 eV lower than that at the Ga site [site (iii)]. Sites B_1 and B_2 yield energies of the order of 2.4–2.7 eV above that for site (ii), illustrating that the isolated H has a greater propensity to saturate dangling bonds. For the minimum energy site (ii), the H-As distance is 1.65 \AA , slightly larger (8%) than the bond length of 1.52 \AA in arsine molecules (AsH_3). The respective distances for H-Be and H-Ga bonds are bigger with H-Be bond being 1.78 \AA while H-Ga is 1.69 \AA [$d(\text{Ga-H}) = 1.12 \text{\AA}$ in gallium monohydride⁴¹], suggesting a weaker interaction compared to the As-H bond for H at the As site [site (ii)].

The following processes are postulated for H-induced passivation of Be acceptors on GaAs(110). First, the compensation reaction involving the free holes with H results in H^+ . Since H^+ has a stronger bias towards bonding with the dangling bond of the As surface atom compared to that for the Ga surface atom as calculated above, possibly due to ionic interactions between H^+ and the more electronegative As as well as the instability of Ga hydride molecules⁴¹ (i.e., Ga-H bonds are unstable), As-H stretching lines are observed from IR experiments with no Ga-H lines observed.^{22,23}

V. CONCLUSION

We have performed total-energy calculations on a microscopic model of a H-Be (acceptor) system on the GaAs(110) surface. Our initial investigation for H on the clean surface shows that for isolated H and H^+ adatoms, they prefer to bond to surface As atoms, consistent with

experimental results from core photoemission studies³⁹ and UPS studies of the H-GaAs(110) system in the low-coverage regime.⁴⁰ As H⁺ has already been observed in *p*-type GaAs,²⁷ its presence as a consequence of the initial compensation reaction with free holes an account for the passivation mechanism of acceptors on the GaAs(110) surface. The microscopic model for this mechanism has the H attached to the dangling bond of the surface As atom close to the acceptor (Be) atom, compatible with the model discussed by Schaefer¹⁴ based on infrared measurements which exhibit strong As-H stretching lines but no Ga-H lines which have not been elucidated up to now.^{22,23} We attribute the absence of bonding between

Ga and H to the preference of H⁺ for bonding with As site as a result of ionic interactions and greater binding energy as As-H bonds are more stable. Such a preference for As-H bonding due to H having a donor level resulting in H⁺ at low coverage may act as a precursor for hydrogen-induced etching of As through the formation and subsequent desorption of AsH₃ at room temperature with increasing coverage leading to surface roughening and the formation of a highly disordered Ga-rich surface.⁴² It would be of great interest to proceed with further investigation of surface ablation due to desorption of AsH₃ as a function of increasing coverage of H.

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