Hydrogen passivation of beryllium in *p*-type GaAs

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(Received 1 June 2001; published 17 October 2001)

The structure, vibration frequencies, reorientation kinetics, and passivation mechanism of the complexes that include hydrogen and Be shallow acceptors in crystalline GaAs have been investigated by an *ab initio* molecular dynamics method. The stable configuration is found for the H atom located near a bond-centered site between the Be acceptor and a nearest neighbor As atom. However, the hydrogen atom tends to move off the trigonal axis by 0.147 Å. The bonding shows that the hydrogen saturates the As atom to leave the Be acceptor threefold coordinated. The vibrations of Be and H are separate. The stretching frequency of hydrogen is similar to an arsine molecule. The present calculations well reproduce the experimental value of reorientation energy for H motion between adjacent bond-centered sites about the Be acceptor in the stable configuration. A good agreement with experiment is also found for the dissociation energy to account for the beryllium passivation by hydrogen. It is H^+ diffusing in and out the stable bond-centered site rather than H^0 in *p*-type GaAs. In tracking the hydrogen, the passivation mechanism of involving a H^+ diffusion cation to neutralize the Be_{Ga}^- acceptor can be resolved.

DOI: 10.1103/PhysRevB.64.195204 PACS number(s): 71.55.Eq, 66.30.Jt, 85.40.Ry, 61.72.−y

Dopant passivation by hydrogen has been known for most elemental and compound semiconductors.[1–5] While there is much technological interest in the passivation of shallow dopants in semiconductors, hydrogen passivates both shallow acceptors and donors in GaAs. Chevallier *et al.* and Johnson *et al.* separately demonstrated hydrogen passivation of shallow donors and acceptors in GaAs first.[6,7] They indicated that passivation is far more extensive for acceptors than donors for comparable net concentrations of dopants in GaAs. A model of electrically inactive complex that includes a hydrogen atom and a shallow dopant is usually suggested for electrically compensation of dopant. The complex is commonly described by the sign H-X_B, where a dopant X is located at a B host site. Once passivated, the accessibility of the dopants is limited. However, the vibrational spectroscopy has provided an excellent probe of the hydrogen-related complexes and helps establish microscopic information for the passivation process. Infrared spectroscopic evidence for the H-Zn_{Ga} complex in GaAs was first shown by observation on the absorption lines of vibration at 2147 cm^{-1} at 7 K.[4] The broadening of the absorption line at higher temperature for the H-Si_{Ga} complex was also investigated in the temperature range between 5.5 and 300 K in GaAs.[8] Thermal stability of the complexes can be simply examined by determining dissociation energy from experimental data. The dissociation energies for several complexes formed by hydrogen and acceptors have been widely reported on 1.45 ± 0.10 eV for H-Si_{As}, 1.35 ± 0.05 eV for H-C_{As}, 1.35 ± 0.10 eV for H-Cd_{Ga}, 1.25 ± 0.10 or 1.33 eV for H-Zn_{Ga}, and 1.15 ± 0.10 eV for H-Be_{Ga}; for several complexes formed by hydrogen and donors on 1.52 ± 0.05 eV for H-Se_{As}, 1.25 ± 0.05 eV for H-Si_{Ga}, and 1.20 ± 0.10 eV for H-Sr_{Ga} in the doping concentration region of $1\sim2\times10^{17}\,cm^{-1}$.[9] An entire understanding of the role of hydrogen in passivation of shallow dopants can certainly address the technological implications and provide the most technological opportunities of hydrogen in semiconductors.

Beryllium is one of the mostly used shallow acceptors in GaAs. The shallow properties and sharp incorporation profile makes it the acceptor of choice in GaAs/AlAs systems grown by conventional molecular beam epitaxy (MBE). Undoped GaAs/AlAs systems are stable for annealing at high temperature up to 900 °C. But it becomes unstable if we dope the GaAs/AlAs systems with Zn acceptors at lower temperature as 600 °C instead. It shows much more favorably doped with Be than Zn on the stability under thermal cycling of the GaAs/AlAs systems.[10–12] At relatively elevated temperatures, hydrogen in the source chemicals inevitably diffuses into GaAs layers and the Be acceptors are easily found deactivated. Nandhra *et al.* first measured the local vibration modes of H-Be_{Ga} complexes at 2037 and 555.7 cm^{-1}.[13] The trigonal symmetry of the H-Be_{Ga} complexes was fully demonstrated by Stavola *et al.*[14] As follows, Veloarisoa *et al.* determined the piezospectroscopic tensor of the H-Be_{Ga} complexes in an external stress.[15] The only theoretical investigation of hydrogen passivation of beryllium in GaAs was performed by Briddon and Jones to find stable hydrogen around the bond-centered position between the Be acceptor and a nearest neighbor As atom in the three clusters of $Ga_{13}As_{13}H_{30}$, $Ga_{22}As_{22}H_{42}$, and $Ga_{26}As_{26}H_{50}$ in which a central Ga atom was replaced by a Be acceptor.[16]

We theoretically investigated H-Be_{Ga} complexes in a crystalline structure of GaAs. The present *ab initio* calculations are performed using Car-Parrinello (CP) molecular dynamics methodology.[17] The valence electrons are described by density-functional theory in the local density approximation (LDA). The norm-conserving pseudopotentials[18] are used and also modified to avoid a Ga "ghost" state.[19] The bulk structural properties of GaAs were truly reproduced.[20] Since

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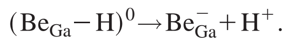
the wave functions of shallow defects are spatially extensive, a larger supercell of 64 atoms is necessarily used. The k points in the first Brillouin zone (BZ) for sampling the electron charge density are those folded into the Γ point of the simple cubic super-cell of 64 host atoms. It has been demonstrated that the Γ-point sampling in the first BZ at such supercell size can effectively reproduce the static and dynamic properties of semiconductors.[21] We have also successfully described the interstitial states and diffusion of hydrogen in GaAs by the Γ-point sampling.[22] The cutoff kinetic energy of plane waves in the wave-function basis is selected for 14 Ry (~9000 plane waves). A faster and complete scheme in the CP method is used for relaxation of the whole crystal as a hydrogen and acceptor atom are embedded in the supercell.[20,22] As the ions move according to Hellmann-Feymann forces in the molecular dynamics evolution, electrons follow closely according to Newtonian equations. A frictionlike force is further imposed to slow down the atoms moving upward on the Born-Oppenheimer surface. It leads to fast relaxation of the atom system for optimization of structures.

Experimentally, the dissociation energy is determined from the dissociation rate of the complexes in the first-order kinetics. The dissociation rate is thermally activated and assumed to be directly proportional to the number of complexes itself. Consequently, an Arrhenius-type temperature dependence is related to the dissociation frequency ν_d in the explicit form

$$\nu_d = \nu_0 \exp(-E_d/KT),$$

where ν_0 is an attempt frequency and E_d is the dissociation energy. The dissociation energy is thus the energy required to fully separate the hydrogen from the dopant. It includes the energy required for break up the bonds formed by the hydrogen atom and the migration energy of the hydrogen species [e.g., H^- in n-type GaAs and H^+ in p-type GaAs (Ref. 22)]. In accordance with the experimental data, the dissociation energy is defined as the energy difference between the initial and the final state of the reaction



$$(\mathrm{Be_{Ga}} - \mathrm{H})^0 \rightarrow \mathrm{Be_{Ga}^-} + \mathrm{H}^+.$$

The H^+ cations released by the complexes are located in their minimum energy sites in p-type GaAs. The dissociation energy is calculated as

$$E_d = [E(\mathrm{Be_{Ga}^-}) + E(H^+)] - \{E[(\mathrm{Be_{Ga}} - H)^0] + E(\mathrm{GaAs})\},$$

where, for example, $E(\mathrm{Be_{Ga}^-})$ denotes the total energy of the 64-atom supercell containing a Be acceptor.

For the calculation of the reorientation energy of hydrogen, we try to simulate an adiabatic trajectory for the H motion around the Be acceptor.[22] Along a specific direction prescribed, the hydrogen is set to very slowly move in a constant speed. All the other atoms in the system relax simultaneously with a frictionlike force. The surplus energy introduced by the constant speed of the hydrogen is then removed in the relaxation. The energy surface along the direction of the movement is then determined.

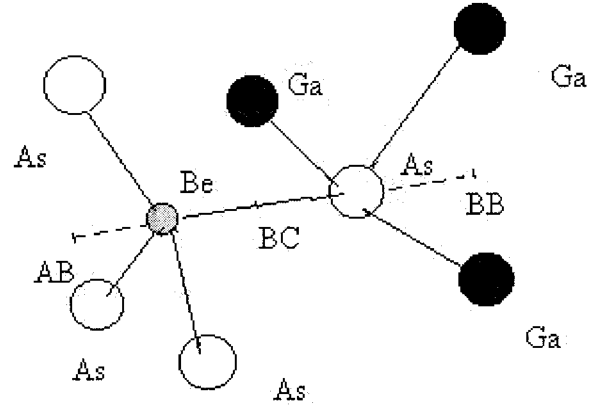


FIG. 1. A schematic diagram showing the favorable sites for hydrogen in the H-$\mathrm{Be_{Ga}}$ complex. BC denotes the bond-centered site between the Be acceptor and the nearest neighbor As host atom; AB the antibonding site of the Be acceptor; BB the back-bonded site of the As host atom. All the sites are referred to the atoms in the $\mathrm{Be_{Ga}}$-As complex.

To investigate the H-$\mathrm{Be_{Ga}}$ complexes, a Be atom was embedded replacing a gallium atom in the supercell of 64 atoms and then an interstitial H atom added. The neighboring H atoms or Be acceptors are apart at a distance of 11.3 Å, which is the double of Bravais lattice constant of GaAs. Three favorable configurations with high symmetry are considered for the H-$\mathrm{Be_{Ga}}$ complex. Referred to the atoms in the trigonal $\mathrm{Be_{Ga}}$-As bond, the H atom is located at the bonded-center (BC) site, the antibonding (AB) site on the $\mathrm{Be_{Ga}}$ side, and the back-bonded (BB) site on the As side, respectively (see Fig. 1). The relative differences in total energies of the three configurations are shown in Table I.

The lowest energy is for the BC configuration. The calculated structural properties are presented in Table II, in which the cluster results by Briddon and Jones are also listed in the second row.[16] The crystalline calculation is more realistic than the clusters due to the periodical boundary conditions. Furthermore, our results benefit from a large separation of defect in a large supercell of 64 atoms and also a thorough relaxation scheme. It is found that the H atom is not definitely located on the axis of the $\mathrm{Be_{Ga}}$-As bond. The total

TABLE I. Relative energies of three favorable configurations for H-$\mathrm{Be_{Ga}}$ complexes. The configurations of complexes are denoted for the symmetry sites occupied by hydrogen. Referred to the atoms in the trigonal $\mathrm{Be_{Ga}}$-As bond, BC is the bond-centered site, AB is the antibonding site of the beryllium acceptor, and BB is the back-bonded site of the beryllium acceptor (i.e., the antibonding site of one of the four arsenic atoms which are nearest neighbors of the beryllium acceptor). The zero of the energy is set at the global minimum.

Configuration	BC (eV)	AB (eV)	BB (eV)
Present	0.0	0.018	0.48
Ref. 16	0.0		0.30

TABLE II. Calculated equilibrium geometry of the BC configuration for hydrogen. In the BC configuration, the beryllium is threefold coordinated and the hydrogen saturates the dangling bond of the arsenic atom to decouple the bonding with the beryllium. The angles between threefold bond of Be-As, and fourfold bond of As-Ga are given in the last two columns. Note that the H passivator is perpendicularly displaced 0.147 Å (see 0.150 Å in Ref. 16) off the trigonal axis.

	H-Be_{Ga} (Å)	H-As (Å)	Be_{Ga}As (Å)	Ga-As (Å)	As-Be_{Ga}-As (deg.)	Ga-As-Ga (deg.)
Present	1.80	1.55	2.22	2.45	96.7	92.7
Ref. 16	1.85	1.52	2.16	2.42	120	117

energy drops by 0.0038 eV for a displacement of the H atom off the trigonal axis by 0.147 Å along a ⟨−110⟩ direction perpendicular to ⟨111⟩. The displacement and the corresponding drop in energy are both very small. The calculation results show that the hydrogen is actually quite free to move in the perpendicular plane across the BC site. In this stable BC configuration for hydrogen, the relaxation energy when the hydrogen is embedded is totally as large as 2.93 eV. Both Be and As move away in the opposite direction from the host position by 0.52 and 0.33 Å, respectively, to expand the Be_{Ga}-As bond (37% greater) for taking in the H atom. It also shows that the H atom lies closer to the As atom than the Be acceptor, giving 1.55 and 1.80 Å for H-As and H-Be_{Ga} bond length, respectively. The 1.55 Å bond length of H-As is very close to the length of H-As bond in an arsine molecule (AsH_3) at 1.52 Å. In addition, the stretching frequency of the H-As bond in an AsH_3 molecule is at 2116 cm^{-1} (Ref. 23) which fits very nicely the infrared data of 2037 cm^{-1} of the H-Be_{Ga} complex.[13] Typical H-X bond stretching frequencies for those p-block elements of X is also reported, and it is a close frequency of 2200 cm^{-1} for the H-As bond.[24] Another evidence for the H-As bond is the 2029 cm^{-1} absorption band observed by Stein in H-implanted GaAs near 200 K.[25] It is clearly indicated that the stretching mode is due to the H-As bond in the disturbance of the nearby Be acceptor. To investigate the vibrational frequencies of the hydrogen, we performed a first-principles molecular dynamics simulation for the supercell at low temperature (~30 K) for about 7.2 p. Then the vibrational frequencies were extracted from fourier transformation of autocorrelation function of the hydrogen velocity. Our stretching frequency is 1700 cm^{-1} which is 16% lower than the infrared data (see 2018 cm^{-1} by Briddon and Jones[16]). The calculated frequency is lowered by 250–500 cm^{-1}, because the LDA calculations systematically underestimate the stretching frequencies.[26] On the other hand, the wagging frequency in our calculations is at 310 cm^{-1} (cf. 301 cm^{-1} by Briddon and Jones[16]). The H-As bond is slightly disturbed by the Be acceptor, as shown by the contours of the valence electrons in Fig. 2. This bonding is further confirmed by both H-As and H-Be bond lengths, which are 3.2 and 30% greater, respectively, than those estimated by using the tetrahedral covalent radii according to Pauling.[27] It suggests that the H atom is primarily bonded to As rather than the Be acceptor. The vibrations of Be and H are decoupled. The stretching mode is mainly due to the H-As bond involved in the complex. In other words, the H interstitial comes to saturate the fourth dangling bond of the As atom and the Be acceptor is left for being only threefold bonded. The electronic level of Be falls into the valence band and is fully occupied resulting in the charge neutrality. Overall, the calculations strongly support the infrared absorption spectrum[13] and the uniaxial stress experiments[14,15] for the H-Be_{Ga} complex, which recommended the stable BC configuration. Being due to the moving of H off the trigonal axis for breaking symmetry in analogy with B-H complex in Si,[28,29] the H-Be_{Ga} complex shows a large sensitivity to external stress in the meantime.

Pavesi *et al.* and we theoretically pointed out that the H atom is amphoteric in charge states depending on the energy of Fermi level in GaAs.[30,22] As a negative U center, the hydrogen behaves as a stable donor near the BC site in p-type material, while as a stable donor near the tetrahedral interstitial site surrounded by four nearest Ga host atoms in the n-type material. The neutral hydrogen has never been a stable species. Therefore, it is the H^+ cation near the BC site involving in the bonding and motion of hydrogen in p-type

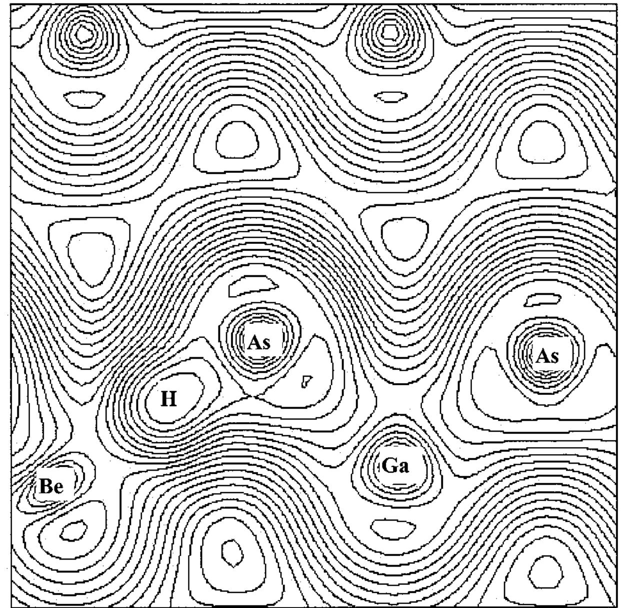


FIG. 2. Contour plots of the valence charge density in [110] plane showing the bonding between atoms in the stable BC configuration for H in Be-doped GaAs. The Be_{Ga}-As bond is 37% greater to make room for H, and the H atom is located 8% closer to As than Be.

GaAs. We have established that the H^+ cation diffuses in the region of high valence electron density following a path of BC-C_{Ga}-BC-C_{As}-BC with an energy barrier of 0.46 eV in *p*-type GaAs, where the symmetry sites C_{Ga} and C_{As}, are at the centers of the rhombus formed between three adjacent Ga and As host atoms and the nearest tetrahedral sites.[22] So far, we have not seen any experiment on the real-time observations of hydrogen drift and diffusion to indicate the occupation of interstitial H^0 site in GaAs. The diffusion species is believed to be H^+ rather than H^0 in *p*-type GaAs. There is also no evidence to indicate that H^0 participates in the passivation process, at least in the case of Be-doped GaAs. It explicitly makes the fact that only the H^+ cation participates in the passivation of Be. The passivation mechanism would involve with the capture of a hole first, i.e., $H^0+h^+\rightarrow H^+$. Subsequently, the capture of a H^+ cation by a Be_{Ga}^- acceptor proceeds as $Be_{Ga}^-+H^+\rightarrow(Be_{Ga}-H)^0$. The large capture radius that characterizes the complex formation is expected of the capture of a positively charged species at a negatively charged acceptor. The reaction equation of passivation can be simply described by $Be_{Ga}^-+H^0+h^+\rightarrow(Be_{Ga}-H)^0$. From this point of view, the stable BC configuration for hydrogen is quite well understood, and the passivation mechanism is unambiguously defined.

The thermal stability of the passivated dopants is obviously of interest if it is to be used in technological applications. As the temperature rises to completely restore the conductivity, the pairs of passivation are dissociated. In *p*-type GaAs, the Fermi energy is such that H^+ is overwhelmingly favored over H^0,[22] the breaking of the bonds formed by hydrogen follows $(Be_{Ga}-H)^0\rightarrow Be_{Ga}^-+H^+$. The H^+ cation released must subsequently diffuse out of the passivated region. The calculated dissociation energy for this configuration is 1.05 eV which is in good agreement with the experimental result of 1.15 ± 0.10 eV.[31]

The diffusion of hydrogen in the complex is entirely controlled by the association and dissociation processes of hydrogen with the Be acceptors. At high temperatures the H atom is quite mobile. Since the trigonal symmetry of the H-Be_{Ga} complexes is lower than the host lattice, the reorientation of the hydrogen is still expected at low temperatures. There are four equivalent BC sites surrounded each Be acceptor. The H atom tends to migrate from a BC site to another BC site of an adjacent bond. A circular path for hydrogen has been suggested for this motion about the Be acceptor.[14,15] The energy surface simulated along the migration path for hydrogen in the [110] plane is shown in Fig. 3 to find that the reorientation energy is 0.32 eV. The energetic equivalence of the hydrogen in these BC sites can be removed by applying an external uniaxial stress. Stavola *et al.* had successfully demonstrated this experiment and found the orientation energy of 0.37 eV.[14] Our calculation comes close enough to verify the reorientation process. Since the relaxation of the H-Be_{Ga} complexes exhibits Arrhenius behavior,[32] the reorientation of hydrogen is thermally activated and does not involve any tunneling motion.

For the other configurations in our discussions, the energy of the *AB* configuration for hydrogen is 0.018 eV higher than the BC configuration. In the proposed configuration, Be is fivefold coordinated and H forms a bond with each of the three As atoms and one with Be. One of the Be_{Ga}-As bonds lengthens to 3.30 Å, caused by the disturbance of hydrogen present at the antibonding site of Be. Another Be_{Ga}-As bond length is 2.58 Å, while the remains are both 2.22 Å. These bonds turn out to be sp^2 instead of sp^3 in character. The character of bonding is very much like the fivefold coordinated Si donor in H-Si_{Ga} complex in *n*-type GaAs.[32] Accordingly, the Be atom relaxes toward the plane of the other three As atoms. For the As atom in the unique Be_{Ga}-As bond, the resulting length of the H-As bond is 1.56 Å. The other two H-As bond lengths are 3.08 and 2.27 Å, respectively. All the three H, Be, and As atoms along the trigonal direction have relaxed out of the [110] plane. The total energy gained by relaxation is 1.6 eV. The H-Be_{Ga} bond has a length of 1.79 Å, which is about 0.41 Å longer than what would have been expected for a H-Be_{Ga} bond from Pauling's tetrahedral covalent radius estimation. It is difficult to imagine how a lengthening H-Be_{Ga} bond of 1.79 Å can be responsible for a stretching frequency as high as the experimental frequency of 2031 cm^{-1}. Finally, the energy of the BB configuration for hydrogen is 0.48 eV higher than the BC configuration. The resulting H-As bond length is 1.57 Å, with the unique Be_{Ga}-As bond lengthening to 3.09 Å. By applying an external uniaxial stress, the orientation of the hydrogen can occur in the H-Be_{Ga} complexes as indicated in Refs. 14 and 15. The measurements of the dichroism decay time at various temperatures after the removal of the stress allow us to estimate the orientation energy and the relaxation. But such orientation processes for GaAs cannot be observed in both AB and BB configurations. This would verify that BC configuration for hydrogen prevails.

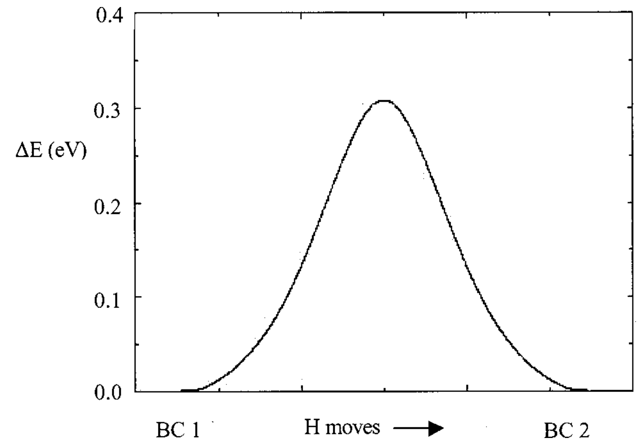


FIG. 3. Total energy changes for the motion of H between adjacent BC sites about the Be acceptor in the stable BC configuration in the [110] plane. The energy barrier is the maximum of the curve, which corresponds to the orientation energy of hydrogen in the H-Be_{Ga} complex.

In summary, we have calculated the total energy and geometry for the stable configuration of hydrogen in the H-Be_{Ga} complex. The hydrogen passivation of the beryllium acceptor preferably begins with the capture of a hole for the

H^0 to result in H^+ cation in *p*-type GaAs. It is then the H^+ cation diffusing in the stable BC site. The neutralization of H^+ with the Be_{Ga}^- acceptor on the host gallium site goes on with the large cross section expected of a Coulomb capture process. The distribution of valence electrons shows that the H passivator is primarily bonded to the As atom rather than the Be acceptor. While there is no significant bonding between H and Be atoms, the stretching frequency of the H-Be_{Ga} complexes is mainly due to the H-As bond. The stretching frequency of hydrogen resembles an arsine molecule. The calculations on the orientation and dissociation energy of the H-Be_{Ga} complexes are respectively in strikingly good agreement with their experimental counterparts to fully make this strong case. It clearly accounts for the passivation mechanism and comes to the conclusion that hydrogen passivation of the Be acceptor is due to complex formation of H-Be_{Ga} and not compensation alone.

A part of the calculations has been carried out at the National Center for High-Performance Computing (NCHC), Taiwan, under National Science Council (NSC) Grant No. NSC 89-2112-M-259-004.

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