Energetics and self-compensation of Li in GaAs

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The structural and electronic properties of lithium substitutional acceptors and interstitial donors in crystalline GaAs are investigated using a density-functional theory-based method. In *p*-type GaAs, Li tetrahedral interstitial (Li^{+}_{TAs}) donors have a low formation energy, which is comparable to that of the acceptors (Li^{-2}_{Ga}) in *n* type, namely, a substitutional Li on the Ga site. The donors enhance the solubility of the acceptors and vice versa. In thermodynamic equilibrium, the incorporation of large amounts of Li will result in severe self-compensation. To examine the kinetics of Li, diffusion mechanisms of Li^{+}_{TAs} and Li^{-2}_{Ga} are explored. Li^{+}_{TAs} is highly mobile with a barrier of 0.43 eV, compared to a large barrier of 2.73 eV for relatively immobile Li^{-2}_{Ga}. We have also investigated complex formation and dissociation between interstitial donors and substitutional acceptors. The mechanism of lithium self-compensation involving two diffusive Li^{+}_{TAs} cations in two stages to neutralize a Li^{-2}_{Ga} anion can be resolved. A comparison with available experiments confirms our findings. The expectation of the results is also consistent with lithium compensation in both strongly extrinsic *p*-type and *n*-type GaAs.

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I. INTRODUCTION

Lithium (Li) has been extensively used as an electrically active chemical probe in the investigation of impurities and intrinsic defects in semiconductors. The interaction of extra defects with Li may significantly influence some of its characteristic properties such as its lattice site, diffusion constant, or dopant character, etc. Such influences are of tremendous practical importance on designing materials to have specific desired properties essential to contemporary technology, once we have this understanding. Thus the main technical applications of Li were based on its interactions with various defects. Li compensated *p*-type Ge,[1–3] as an example, was used in the fabrication of large Ge γ detectors. Li also compensated *p*-type Si.[4,5] In contrast to the case of Ge or Si, where Li is simply an interstitial donor, the behavior of Li in GaAs is strikingly different. Understanding defect configurations in heavily doped GaAs is of interest in the modern electronic devices, such as Gunn oscillators and semiconductor lasers. Considerable information on defect configurations may be acquired by investigating the behavior of Li diffused into GaAs. Li was found not only to compensate both *p*- and *n*-type GaAs, but also to distinctly self-compensate.[6–13] The activation of both donors and acceptors are specifically restrained by the self-compensation of Li, which is indicative of the complexity of Li defects in GaAs.

Self-compensation of Li in GaAs was first detected by Fuller and Wolfstirn.[6,7] They found that after saturation with Li (350–1100 °C), the materials were essentially compensated in generally high resistivity *p* type (>10 Ω cm). However, upon heating (350–600 °C) after removal of the Li source, the same materials changed to low resistivity *p* type (<0.2 Ω cm). Several attempts were henceforth tried in order to determine the Li defects for self-compensation in GaAs. Levy and Spitzer identified the localized-vibrational-modes (LVM) absorption bands due to five different Li complexes involved Li interstitials and vacancies.[11,14] Norris and Narayanan observed the tetrahedral morphology of the precipitation of Li and the prismatic dislocation loops of the vacancy type in Zn-doped material by transmission electron microscopy.[15] Isolated Li interstitials or substitutionals were not identified in experiments. Butcher *et al.* examined the defect states by optical deep level transient conductance spectroscopy (ODLTCS) and deep level transient spectroscopy (DLTS) to point out that there were two electron traps in addition to EL2.[16] Recent experiments by Gislason *et al.* verified the positively charged Li drifting in the electrical field, and derived the intrinsic diffusivity of Li with a migration energy of 0.67 eV.[17,18] Positrons trapping at both gallium vacancy and antisite defects were found to increase in both in- and out-diffusion of Li by Arpianinen *et al.*[19] Yet few of these defects have been established with any reasonable and cogent certainty. Thus far the exact self-compensation mechanism of Li in GaAs still remains unclear.

II. METHODS

The present *ab initio* calculations were performed using the Car-Parinello (CP) molecular dynamics methodology.[20] The valence electrons are described by density-functional theory in the local density approximation (LDA). The norm-conserving pseudopotentials are used and also modified to avoid a Ga "ghost" state.[21] The cutoff kinetic energy for the plane wave basis was 14 Ry (~9000 planes waves). Tests for pure GaAs show that these pseudopotentials very well reproduce structural properties from previous theoretical and experimental results.[22] Calculations for defects were carried out in a large supercell that contains 64 atoms in the case of

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perfect crystal. The k points in the first Brillouin zone (BZ) for sampling the charge density of valence electrons are those folded into the Γ point of the simple cubic supercell of 64 atoms. The reproduction of the static and dynamic properties of semiconductors by the Γ-point sampling at such a supercell size was proven to be effective.[23] A faster and thorough scheme in the CP method is used for relaxation. As the ions move according to Hellmann-Feymann forces in the evolution of molecular dynamics, electrons follow closely according to Newtonian equations. A frictionlike force is imposed to slow down the atoms moving upward on the Born-Oppenheimer surface, so it leads to a fast relaxation of the atom system for optimization of static structures. This method was very successfully exercised in describing the incorporation and diffusion of hydrogen in GaAs.[24]

The incorporation of impurity in a semiconductor depends on the sources of atoms involved in the process. In a thermodynamic process, the abundances of the source atoms are described by the chemical potentials. Moreover, the solubility of an ionizing impurity in a semiconductor is affected by the electron and hole concentrations. For example, the energy required to incorporate a donor impurity is reduced by the energy liberated in the ionization of the donor, i.e., by an electron falling from the donor level to the Fermi level. Thus, in addition to the chemical potential, the formation energy of an ionized impurity in a semiconductor is also determined by the Fermi level. The Fermi level is not an independent parameter, but is determined by the charge neutrality. We calculated the total energy of a supercell embedded with Li for various configurations. The formation energy of a defect X in a charge state q, denoted by X^q, is then

$$E_f(X^q) = [E(\mathrm{GaAs}{:}X^q) - E(\mathrm{GaAs})] - \sum_y n_y \mu_y + qE_F, \quad (1)$$

where $E(\mathrm{GaAs}{:}X^q)$ and $E(\mathrm{GaAs})$ are the total energies of the supercell embedded with and without a defect X^q, n_y is the number of atom increased in the defect system, μ_y is the corresponding chemical potential (y=Ga, As, and Li), and E_F is the energy of Fermi level. The chemical potentials for Ga and As must satisfy the equilibrium conditions with GaAs:$\mu_{Ga}+\mu_{As}=\mu_{GaAs}$. Once one of μ_{Ga} and μ_{As} is determined, the stoichiometry of the system is characterized only by the other. In other words, we have assumed that the atom supply is in equilibrium with distant reservoirs, with which y atoms are exchanged and whose energies at $T=0$, by definition, are the chemical potentials. In the following, we will use the chemical potentials of solid Ga and Li in their equilibrium crystal structures. By fixing the chemical potentials, the formation energy becomes solely a function of the Fermi energy. Considering the chemical potential of solid Li is in accordance with experiments in the saturation of Li by Fuller and Wolfstirn.[6,7]

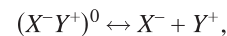
In the dilute limit, the concentration $C(X^q)$ of a defect X^q at thermal equilibrium temperature T, is approximately determined by

$$C(X^q) = gN_s \exp[S_f(X^q)/k]\exp[-E_f(X^q)/kT], \quad (2)$$

where g is the degeneracy factor representing the number of possible configurations for a defect on the same site, N_s is the number of available sites that the defect can be incorporated on, k is the Boltzmann constant, and S_f is the formation entropy. An *ab initio* calculation of the formation entropy is currently prohibitively expensive. In low temperature, or in case entropy, contributions tend to cancel to some extent when comparing relatively free energies, the entropic contributions are small enough to be neglected.[25,26] Otherwise, we use a typical value of $6k$ for all the defects, which is the result of a recent extensive calculation for vacancies and interstitials in Si.[27] This approximation was also used in Refs. 22 and 28. The equation thus shows that the defect with low formation energy will occur in high concentration. As temperature increases, the concentration of the defect increases. For charged defects, the inability of LDA to reproduce semiconductor band gaps leads to an overestimate of their concentrations.

The migration energy (or diffusion barrier) is the difference between the energy of the saddle point and that of the stable configuration. For any diffusion mechanism, there is a specific path for the diffusing atom to follow. The position of the saddle point can be only determined by considering the symmetry along the path. We used an "adiabatic trajectory" technique whenever a migration barrier is needed.[24] Along the specific path under consideration, the diffusing atom moves with a constant, small speed (e.g., thermal speed at 300 K), while the remaining atoms continuously relax with a frictionlike force in response to its motion. The excess energy introduced by the constant speed of the diffusing atom is then removed in the relaxation. Thus the energy contour along the direction of the movement can be depicted.

The dissociation energy of a complex is the energy required for fully separating the constituent ions and restoring the electrical conductivity. One may therefore define the dissociation energy as the difference between the two reaction activation energies associated with that of the dissociation reaction. To calculate the dissociation energy of the complex, such as $(X^-Y^+)^0$, based on the reaction equation



$$(X^-Y^+)^0 \leftrightarrow X^- + Y^+,$$

one has to use the following formula:

$$E_d = [E(X^-) + E(Y^+)] - \{E[(X^-Y^+)^0] + E(\mathrm{GaAs})\},$$

where, e.g., $E(X^-)$ denotes the total energy of a 64-atom supercell containing an isolated foreign anion X^- at its stable equilibrium site.

III. RESULTS AND DISCUSSION

A. Stable configurations and diffusions of Li in the lattice

The stable sites and charge states of Li are examined by calculating the formation energy at ten different sites with high symmetry. These sites include nine interstitial sites and a Ga-substituional site. Eight of the interstitial sites, shown in Fig. 1, are located in the (110) plane. The M site is not in the (110) plane, but located midway on the axis connecting BC with the nearest Hex sites. It is informative to plot the formation energy of Li as a function of the Fermi energy E_F in order to examine the behavior of defects when the doping

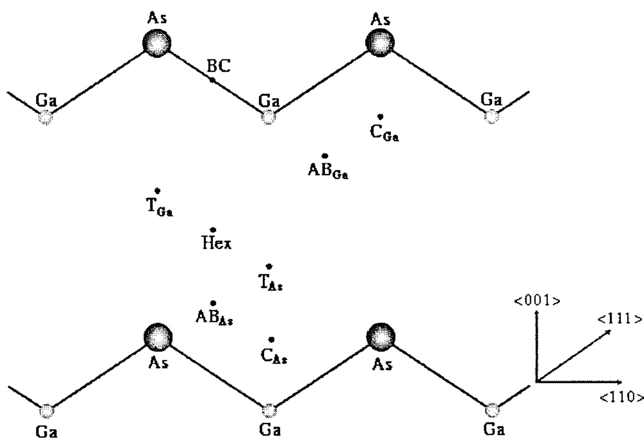


FIG. 1. A schematic plot of interstitial sites of high symmetry for Li in (110) plane in the zinc-blende structure of GaAs. The horizontal direction is in the $\langle 110 \rangle$ direction and the vertical direction in the $\langle 001 \rangle$ direction. The eight interstitial sites are a tetrahedral site coordinated by four Ga atoms (T_{Ga}) (two of which are out of the plane of the figure and are not shown), a tetrahedral site coordinated by four As atoms (T_{As}) (two of which are out of the plane of the figure and are not shown), an antibonding site nearest to a Ga host (AB_{Ga}), an antibonding site nearest to a As host (AB_{As}), a center site of the rhombus formed between three nearest Ga atoms and the T_{As} site (C_{Ga}), a center site of the rhombus formed between three nearest As atoms and the T_{Ga} site (C_{As}), a bond-centered site (BC) halfway between two next neighboring host atoms, and a hexagonal site (Hex) halfway between two next neighboring tetrahedral interstitial sites.

level changes. The incorporated Li is commonly described by the sign Li_X^y, where the subscript letter X stands for the symmetry site occupied and the superscript letter y the corresponding charge state. Figure 2 shows the formation energy of Li at the stable symmetric sites in comparison to that of the Ga vacancy as a function of Fermi energy in Ga-rich conditions, in which the chemical potentials of solid Ga and Li are assumed. Li is a double acceptor at the Ga-substitutional site. However, it is simply a single donor at any interstitial site. We have checked all the highly symmetric interstitial configurations, and the only stable site is T_{As}; Li at BC, C_{As}, AB_{As}, M, Hex, and T_{Ga} all relax to rest at T_{As}, respectively, while T_{Ga} is a metastable saddle-point configuration. So, in the state of single atom, Li can be incorporated at the interstitial T_{As} site as a Li_{TAs}^+ donor in p type, and at the Ga-substitutional site as a Li_{Ga}^{-2} acceptor in n type.

As expected, Li_{TAs}^+ is quite mobile. We found Li_{TAs}^+ diffuses by the interstitial mechanism along the $T_{As}-Hex-T_{Ga}-Hex-T_{As}$ path. An adiabatic trajectory of energy for the motion of interstitial cation Li_i^+ is drawn along the interstice in Fig. 3. As the cation Li_i^+ was moving along the interstitial path, the energy monotonously rose to the maximum at T_{Ga}. The maximum of the trajectory corresponds to the saddle point with a migration energy barrier of only 0.43 eV. The small migration barrier implies that Li_i^+ can swiftly diffuse in the interstice. It has been pointed out that the gallium vacancy, V_{Ga}^{-3}, is one of the favorable native defects in n type.[22]

As more Li_i^+ are supplied, Ga vacancies are favorably generated to recombine with the interstitial donors forming

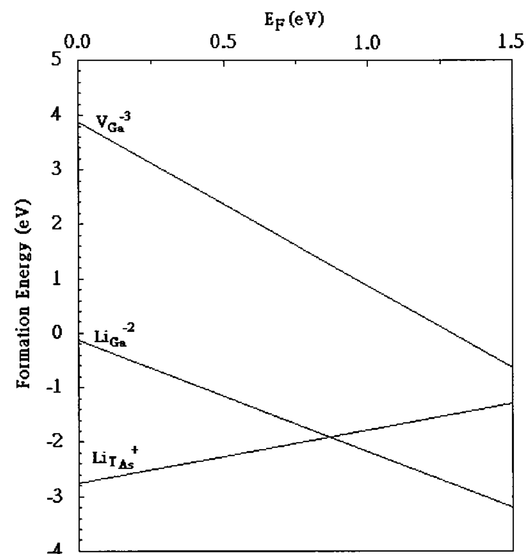


FIG. 2. Formation energies as a function of the Fermi energy (E_F) for ionized Li atom in Ga-rich conditions. The solubility limit of Li is determined by the solid Li. For completeness, the formation energy of Ga vacancy, V_{Ga}^{-3}, is also included. The slopes of the defect formation energies characterize the charge states (e.g., a slope of +1 indicates a +1 charge state, corresponding to a donor, while a slope of −1 indicates a −1 charge state, corresponding to an acceptor). $E_F=0$ corresponds to the top of the valence band.

Li_{Ga}^{-2} acceptors. When we compare the energy of a distant $(\mathrm{Li}_{TGa}^+-V_{Ga}^{-3})^{-2}$ pair with that of Li_{Ga}^{-2}, the latter is always vastly favored energetically by 2.37 eV. Therefore, Li_i^+ has the tendency to recombine into a Ga vacancy. On the contrary to Li_i^+, Li_{Ga}^{-2} is relatively immobile. We found that Li_{Ga}^{-2} diffuses by the dissociative mechanism, or Frank-Turnbull mechanism, which was originally suggested for the diffusion of Cu in Ge.[29] The dissociative mechanism assumed that once Li_{Ga}^{-2} is formed, a certain fraction of Li_{Ga}^{-2} becomes interstitial to form Li_i^+ through the reaction $\mathrm{Li}_{Ga}^{-2}\rightarrow\mathrm{Li}_i^+ + V_{Ga}^{-3}$ with a T_{Ga} as the saddle point. Thereafter, Li_i^+ can further swiftly diffuse away in the interstice and react with V_{Ga}^{-3} for recombination there. The energy barrier of migration is the same energy in value as in the recombination process. The

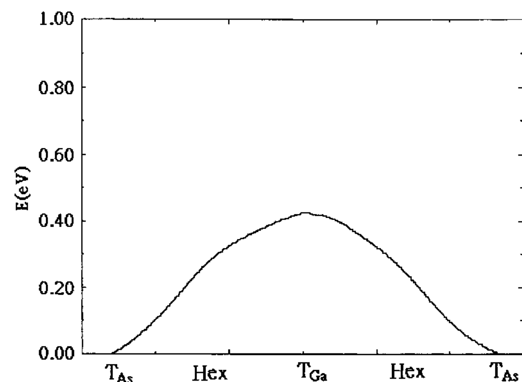


FIG. 3. Total energy changes for the motion of the interstitial cation Li_i^+ along the interstice path $T_{As}-Hex-T_{Ga}-Hex-T_{As}$ in the (110) plane. The maximum of the curve, corresponding to migration energy, is found at T_{Ga}.

barrier of noticeable 2.37 eV implies Li_{Ga}^{-2} firmly stays at a relatively high temperature.

Therefore, whenever Li is incorporated chemically, the interplays of substitution and interstitial are determined by the Fermi energy. Since the law of mass action must be applied to equilibrium situations, it has been possible to obtain an increase in the solubility of Li acceptors by doping with donors and vice versa. From these results, we may speculate that Li is not a dopant but may compensate either donors or acceptors. The compensation between the electron and the hole will also reduce the concentrations of the amphoterics. Such amphoterics are stably formed to directly self-compensate only when the concentrations of the amphoterics are the same. Apparently, it is not the case for Li.

Both Li and H are among the fastest diffusing impurities in group-I elements in GaAs. Nevertheless Li behaves somewhat differently from H in GaAs. H has long been known as an all-purpose compensator; it saturates dangling bonds at surfaces, vacancies, and grand boundaries, and compensates a number of electrically active impurities, e.g., both shallow donor and acceptor in virtually all semiconductors. Not being substitutional, H shows the amphoteric character only by occupying the interstitial sites. The stable H donor is H_{BC}^{+} in p type, while the stable H acceptor H_{TGa}^{-} in n type.[24] H_{BC}^{+} diffuses in the high electron density region along the $BC-C_{Ga}-BC-C_{As}-BC$ path with a barrier of 0.45 eV in p type, but H_{TGa}^{-} diffuses in the low electron density region along $T_{Ga}-Hex-T_{As}-Hex-T_{Ga}$ with a slightly larger barrier of 0.55 eV in n type. Both H_{BC}^{+} and H_{TGa}^{-} are mostly mobile. The donor level of Li_{TAs}^{+} is deep at 0.74 eV above the valence band, while the donor level of H_{BC}^{+} is shallow at a value of 0.22 eV above the valence band. As for the stable acceptor states, the acceptor levels of Li_{Ga}^{-2} and H_{TGa}^{-} are resonant within the valence bands.

B. Complexes between interstitial Li and substituional Li

As can be seen by the effect of self-compensation, Li_{TAs}^{+} and Li_{Ga}^{-2} are not possibly isolated, and Li complexes must be inherently formed by Li_{Ga}^{-2}, Li_{TAs}^{+}, or possibly some other Li interstitial, e.g., Li_{TGa}^{+}. The desirable complex would be relevantly in the structure of a congregation of Li ions bonded for neutralization as a whole. The calculation results for the formation energies of Li complexes as a function of Fermi level are displayed in Fig. 4 in Ga-rich conditions. The results show that the principal acceptor is $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ instead of Li_{Ga}^{-2} in n type, firstly. Resemblant to $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ is $(Li_{TGa}^{+}Li_{Ga}^{-2})^{-}$. The distance between the two Li atoms in $(Li_{TGa}^{+}Li_{Ga}^{-2})^{-}$ is 0.36Å smaller than that in $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$. But the formation energy of $(Li_{TGa}^{+}Li_{Ga}^{-2})^{-}$ is 0.10 eV higher than that of $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$. The stability of $(Li_{TGa}^{+}Li_{Ga}^{-2})^{-}$ may be slightly weakened by the metallike bonding between the Li atoms. The formation energy of the $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ is 0.95 eV lower than that of Li_{Ga}^{-2} in n type, but 0.20 eV higher than that of Li_{TAs}^{+} in p type. Thus $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ instead of Li_{Ga}^{-2} is the principal acceptor, as suggested with the 0.023 eV ionization level for the doublet by Fuller and Allison.[30]

Nevertheless, the remarkable, simple results in Fig. 4 show that the inherent Li defect is actually in the triplet form

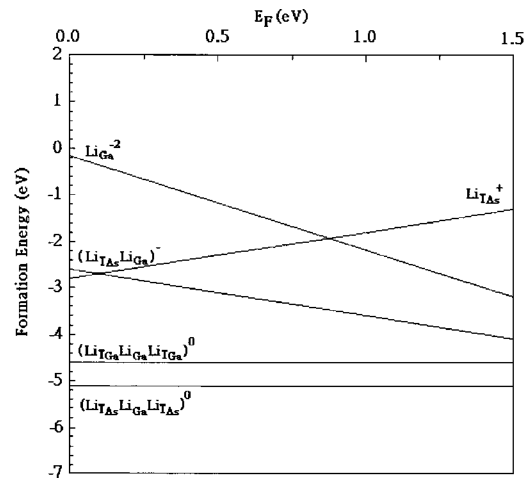


FIG. 4. Formation energies as a function of the Fermi energy for favorite Li complexes in Ga-rich conditions. The solubility limit of Li is determined by the solid Li. The formation energy of Li_{TAs}^{+} and Li_{Ga}^{-2} is also included for comparison. The line $(Li_{TGa}^{+}Li_{Ga}^{-2})^{-}$, which is 0.10 eV above the line $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$, is not shown. $E_F=0$ corresponds to at the top of the valence band.

of $(Li_{TAs}^{+}Li_{Ga}^{-2}Li_{TAs}^{+})^{0}$. In the triplet, the Li_{TAs}^{+} has four As nearest neighbors and a Li_{Ga}^{-2} as a second-nearest neighbor, as shown in Figs. 5(a) and 5(b). The two Li_{TAs}^{+} donors in Fig. 5(a) are farther apart than those in Fig. 5(b) by 1.56 Å. The energy of the structure in Fig. 5(b) is higher than that in Fig. 5(a) by about 0.06 eV, which is within our calculation uncertainty. In the following discussion we will only refer to the structure in Fig. 5(a) as the triplet considered. The formation energy of $(Li_{TAs}^{+}Li_{Ga}^{-2}Li_{TAs}^{+})^{0}$ is 2.35 eV lower than that of Li_{TAs}^{+} in p type, while 1.02 eV lower than that of $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ in n type. Since the degeneracy factor g indicates that the possible configurations of the $(Li_{TAs}^{+}Li_{Ga}^{-2}Li_{TAs}^{+})^{0}$ complex is four, and pairing occurs rapidly upon cooling, the concentrations of the Li complexes are generally affected by the exponential factor of the formation energy. So upon quenching from the saturation temperature of the species, Li_{TAs}^{+} and $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ are present together with the precipitated phase containing Li. In other words, the Li triplet complex is far more energetically favorable than any other. After a full relaxation, each Li_{TAs}^{+} has moved 0.14 Å (6.0%) closer directly toward the center of Li_{Ga}^{-2} along the principal symmetry axis connecting the three Li ions, and each of the four As nearest neighbors has also moved closer toward Li_{Ga}^{-2} in the breathing mode by a distance of 0.10 Å (4.3%). The atomic relaxation is accompanied by an energy gain of 0.41 eV.

Figure 6 shows the corresponding valence charge density of the triplet. Nearly 0.3e more charge is depleted from around the cation As to participate in the new Li bonds which are the forms of Li–Li and Li–As. The maximum charge density in the Li–As bond is slightly larger than that of a pure Ga–As bond. In other words, a larger mismatch between cation and anion in the valance region gives rise to a slightly higher ionicity for the Li–As bond than a pure Ga–As bond. In response to the charge transfer, the 3d core level of cation As must shift to a weaker binding energy when the triplet is formed.

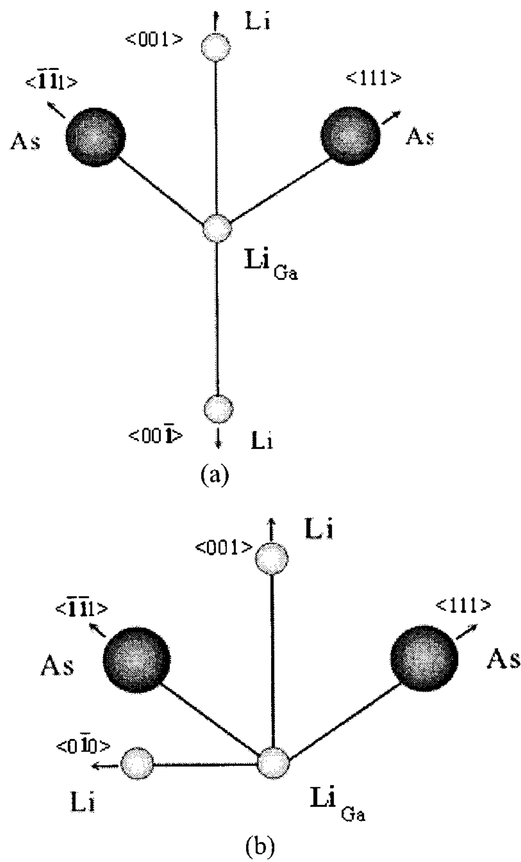


FIG. 5. A schematic plot of (110)-plane view of the triplet $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}$. Views along the $\langle 111\rangle$, $\langle 001\rangle$, $\langle 00\bar{1}\rangle$, $\langle \bar{1}\bar{1}1\rangle$, and $\langle 0\bar{1}0\rangle$ directions are shown. The Li atom at the center of the system is located at the Ga-substitutional site, while the other two Li atoms are at the next neighboring T_{As} sites in the interstices. The distance between the two Li atoms at the separate T_{As} sites is 5.34 Å for (a) and 3.77 Å for (b).

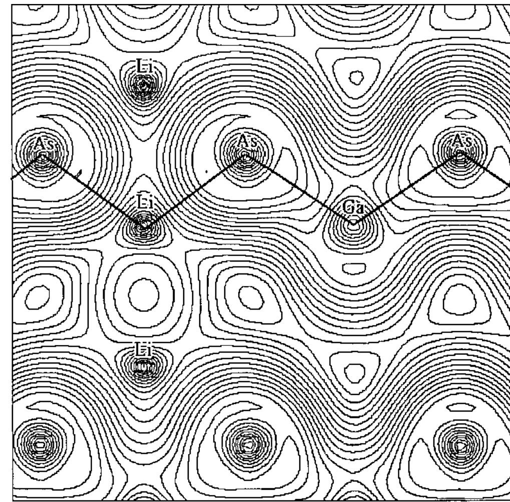


FIG. 6. Contour plots of the valence charge density in (110) plane for the triplet complex $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}$ in Fig. 5(a). An original zigzag bonding chain and some related atomic positions are indicated for reference. The triplet is centered at the left bottom corner of the zigzag chain indicated.

Another favorable configuration of Li triplet is similar to that in Fig. 5 except that two T_{Ga} sites in the same interstice channel are considered for Li interstitials. The configuration is denoted by $(\mathrm{Li}_{TGa}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TGa}^{+})^{0}$ in which each Li_{TGa}^{+} is associated with a Li_{Ga}^{-2} in a (110) plane. The two Li_{TGa}^{+} donors are symmetrical with respect to Li_{Ga}^{-2}. Originally it was a model constructed for the associated Mn at the Ga-substitutional site and two Li interstitials in GaAs by Ref. 12 In the triplet, Li_{Ga}^{-2} moves 0.33 Å off the trigonal axis downward along the principal symmetry axis. Each Li_{TGa}^{+} also moves 0.37 Å (15.9%) closer toward Li_{Ga}^{-2} in the direction of compression. Caused by the disturbance of Li_{TGa}^{+}, each of the Li_{Ga}–As bonds in the (110) plane shortens by 0.24 Å (10.3%) while each of the other two extends by 0.02Å (0.8%). The atomic relaxation energy is totally summed up to 0.92 eV. But the formation energy of $(\mathrm{Li}_{TGa}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TGa}^{+})^{0}$ is 0.34 eV higher than that of $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}$.

C. The mechanism of Li self-compensation

The formation of the electrically inactive triplet $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}$ is made responsible for the self-compensation of Li. As indicated by Gislason *et al.*, the diffusion species of Li in GaAs is the interstitial lithium cation Li_{i}^{+}.[17] The self-compensation mechanism would involve the capture of a hole for Li first, i.e., $\mathrm{Li}_{i}^{0}+\mathrm{h}^{+}\rightarrow\mathrm{Li}_{i}^{+}$. The cation Li_{i}^{+} is predicted to freely diffuse in the interstice until it recombines exothermically with a Ga vacancy producing Li_{Ga}^{-2}, as described by $\mathrm{Li}_{i}^{+}+V_{Ga}^{-3}\rightarrow\mathrm{Li}_{Ga}^{-2}$. Subsequently, the first capture of a cation Li_{TAs}^{+} by the anion Li_{Ga}^{-2} proceeds as $\mathrm{Li}_{TAs}^{+}+\mathrm{Li}_{Ga}^{-2}\rightarrow(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}$. The second capture of a cation Li_{TAs}^{+} in the next neighboring interstice channel by the doublet anion $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}$ must instantly follow as $\mathrm{Li}_{TAs}^{+}+(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}\rightarrow(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}$ to make for self-compensation. The experimental observation by Fuller and Wolfstirn already showed us that the introduction of two Li atoms caused a loss of one electron corresponding to a $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}$ doublet, and such a $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}$ complex can be stable up to 400 °C at a sufficiently high concentration of Li ($\sim 10^{19}$ cm^{-3}).[6,7] The formation of the triplet complex could just consistently explain the distinctive self-compensation.

The thermal stability of the $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}$ complex is of consequence if it is to be used in technology applications. As the temperature rises to fully restore the conductivity, the triplet complexes are dissociated. The dissociation of the triplet, $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}\rightarrow(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}+\mathrm{Li}_{TAs}^{+}$, requires a dissociation energy calculated as 0.28 eV. The dissociation energy of the $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}$ doublet product will follow on the instant if the temperature remains high. The dissociation energy of $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}$, according to the reaction, $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}\rightarrow\mathrm{Li}_{Ga}^{-2}+\mathrm{Li}_{TAs}^{+}$, is calculated as 0.30 eV. Therefore, both $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2}\mathrm{Li}_{TAs}^{+})^{0}$ and $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}$ complexes are equally thermally dissociative. The steady increase in the hole mobility with Li removal at high temperature in accordance with the two consecutive dissociations was proved in the experiment by Fuller and Wolfstirn.[7] The observation of the change in the mobility further evidenced that $(\mathrm{Li}_{TAs}^{+}\mathrm{Li}_{Ga}^{-2})^{-}$,

not Li_{Ga}^{-2}, is the principal acceptor observed. It would not be expected if the principal acceptor were Li_{Ga}^{-2} species. In the processes of the dissociations, Li_{TAs}^{+} has to be neutralized or diffused out of the p-type region in order to activate $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ and Li_{Ga}^{-2} acceptors. The possibilities are the diffusion of Li_{TAs}^{+} into the substrate, to the surface, or to the extended defects which occur in high concentration in GaAs.[31,32] After the dissociations of $(Li_{TAs}^{+}Li_{Ga}^{-2}Li_{TAs}^{+})^{0}$ and $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$, Li_{Ga}^{-2} acceptors are left behind. The abundance of Li_{Ga}^{-2} acceptors, therefore, attributes to the low resistivity *p* type after thermal annealing.[6,7]

Li was able to compensate Te, S, Se, and Si donors in *n*-type GaAs (Refs. 8–10) and Zn, Cd, Mn, and Mg acceptors in *p*-type GaAs.[9,11–13] The localized-mode spectra had been examined and attributed to the Li-dopant pairs, e.g., Li-Te (with a Te concentration of 5×10^{18} cm^{-3}) and Li-Zn (with a Zn concentration of 1.4×10^{19} cm^{-3}) etc. in Ref. 9. The complexes in the structure of $Li_{Ga}^{-}Te_{As}^{+}$ and $Li_{TAs}^{+}Zn_{Ga}^{-}$ pairs would be expected in each separate case. Pairing between Li and the dopant would certainly cause the enhancement of the solubility in equilibrium for either Te in *n* type or Zn in *p* type. In *n* type the solubility of Li_{TAs}^{+} will be reduced by Te_{As}^{+}. However the solubility of Li_{Ga}^{-2} will be enhanced by Li_{TAs}^{+} and Te_{As}^{+}. In *p* type the solubility of Li_{Ga}^{-2} will be reduced by Zn_{Ga}^{-}, while the solubility of Li_{TAs}^{+} will be enhanced by Li_{Ga}^{-2} and Zn_{Ga}^{-}. Li_{TAs}^{+} and Li_{Ga}^{-2} will persist in *p*- and *n*-type GaAs, respectively, if those dopants are not overcompensated. All these experimental results undoubtedly demonstrated the amphoteric character of Li in GaAs, as fully displayed in Fig. 2.

IV. SUMMARY

We have shown that Li turns out not to be a thermally stable dopant. Being mostly positively charged, Li behaves as one of the shallowest donors. Li enters the crystal and rapidly diffuses as Li_{i}^{+} in the interstice with a mere energy barrier during saturation. Li_{i}^{+} finds itself stable at the tetrahedral site coordinated by four As atoms as Li_{TAs}^{+} in *p* type. As more Li_{i}^{+} is supplied, V_{Ga}^{-3} are favorably generated. The diffusing Li_{i}^{+} reacts therein with V_{Ga}^{-3} to produce Li_{Ga}^{-2}. The diffusion barrier of Li_{Ga}^{-2} is so high that it is hardly mobile. Consequently, the capture of a Li_{TAs}^{+} cation by a Li_{Ga}^{-2} anion proceeds to form the principal $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ acceptor. Another capture of a Li_{TAs}^{+} cation by a $(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ anion leads to form a stable $(Li_{TAs}^{+}Li_{Ga}^{-2}Li_{TAs}^{+})^{0}$ complex, which is energetically commending either in *p* or *n* type. Two stages of reaction involving two Li_{TAs}^{+} cations captured by a Li_{Ga}^{-2} anion, $Li_{TAs}^{+}+Li_{Ga}^{-2}\rightarrow(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}$ and $Li_{TAs}^{+}+(Li_{TAs}^{+}Li_{Ga}^{-2})^{-}\rightarrow(Li_{TAs}^{+}Li_{Ga}^{-2}Li_{TAs}^{+})^{0}$, are thus distinguished. The interaction between the Li-related ions is elucidated. Quenching to room temperature after high temperature diffusion of Li, extra mobile Li_{TAs}^{+} will willingly precipitate, leaving relatively immobile excess Li_{Ga}^{-2} for bringing about the slightly *p*-type self-compensation.

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