As vacancies, Ga antisites and Au impurities in Zincblende and Wurtzite GaAs nanowire segments from first principles

Yaojun A. Du,1 Sung Sakong,1 and Peter Kratzer1

1Fakultät für Physik and Center for Nanointegration (CENIDE), Lotharstraße 1, 47048 Duisburg, Germany

In this paper some specific issues related to point defects in GaAs nanowires are addressed with the help of density functional theory calculations. These issues mainly arise from the growth of nanowires under conditions different from those used for thin films or bulk GaAs, such as the co-existence of zincblende and wurtzite polytypes, the use of gold particles as catalyst, and the arsenic-limited growth regime. Hence, we carry out density-functional calculations for As vacancies, GaAs antisites, and Au impurities in ZB and WZ GaAs crystals. Our results show that As vacancies can diffuse within in a ZB GaAs crystal with migration barriers of ∼1.9 eV. Within WZ GaAs, As vacancy diffusion is found to be anisotropic, with low barriers of 1.60 up to 1.79 eV (depending on doping conditions) in the ab-plane, while there are higher barriers of 2.07 to 2.44 eV to diffuse along the c-axis. The formation energy of Au impurities is found to be generally much lower than those of arsenic vacancies or GaAs antisites. Thus, Au impurities will be the dominant defects formed in Au-catalyzed nanowire growth. Moreover, we find that it is energetically more favorable by 1 to 2 eV for an Au impurity to replace a lattice Ga atom than a lattice As atom in GaAs. An Au substitutional defect for a lattice Ga atom in ZB GaAs is found to create a charge transfer level in the lower half of the band gap. While our calculations locate this level at \( E_v + 0.22 \) eV, taking into account the inaccuracy of the density functional that ought to be corrected by a downshift of \( E_v \) by about 0.2 eV results in good agreement with the experimental result of \( E_v + 0.4 \) eV.

PACS numbers:
Keywords: GaAs nanowire, vacancy diffusion, intrinsic defects, Au impurities, density-functional calculation

I. INTRODUCTION

Semiconductor nanowires have been emerging as a promising building block for various nano-devices. These potential applications include light emitters, solar cells, and microelectronics. All these applications require such a prerequisite that it is possible to keep the concentration of intrinsic defects and impurities in the nanowires below a given threshold so as to enable long exciton lifetimes and to avoid unintentional doping due to electrically active impurities. In recent years, many experimental efforts have been devoted to fast and controllable growth of nanowires that is desired for reliable devices; and a gold nanoparticle is often used as a catalyst to promote the growth of GaAs nanowires. However, an Au droplet that accelerates an underneath growing nanowire can also leave impurities within the GaAs nanowire. Previous experimental efforts have focused on characterizing Au defect levels within a GaAs crystal. Moreover, experimental studies employing X-ray energy-dispersive spectroscopy indicate deviations from stoichiometry in the nanowires close to the growth zone, and thus point to the abundant intrinsic defects, in addition to Au impurities, in GaAs nanowires. While carrier lifetimes in core-shell nanowires from Au-free self-catalyzed growth were found to be much longer than in nanowires from Au-catalyzed growth, they still fall short of the values reported for bulk samples by several orders of magnitude. This may indicate a higher level of growth-related intrinsic defects (as compared to bulk) even in Au-free nanowires.

The focus of our interest is the defects that could be formed in nanowire growth below the metal nanoparticle. While the most abundant defect in low-temperature grown bulk GaAs is the As antisite, we expect this defect not to play a role under the more Ga-rich growth conditions beneath a metal catalyst particle. It is known that near the melting point and under the conditions typical of liquid-phase epitaxy, As vacancies are the dominant defects in GaAs. Furthermore, under As-deficient conditions, the As lattice site might remain unoccupied (As vacancy \( V_{As} \)), it could be occupied by gallium (Ga antisite \( Ga\_{As} \)), or, in case of growth with a gold catalyst, may be occupied by an Au atom (\( Au\_{As} \)). Since there is a general interest in possibly detrimental effects of Au on the properties of GaAs nanowires, we include \( Au\_{Ga} \) defects into our study.

In this context, one has to consider that the effective growth conditions for the nanowire material are probably very different from the moderately arsenic-rich conditions commonly used in GaAs thin film growth. This is due to the following reasons: In nanowire growth, material deposited from the vapor phase onto the substrate, the sidewalls and the metal nanoparticle can reach the interfacial area between the nanowire tip and the particle via surface diffusion or diffusion through the liquid metal particle. It is clear that sufficient Ga atoms can reach the interfacial growth zone at the nanowire tip, since the catalyst particle actually consists of a Au-Ga alloy. The situation is less clear concerning the As supply, since the low-pressure solubility of As in gold is low (in Au-catalyzed growth), or a high high temperature leads to As loss (in self-catalyzed growth). In these cases, one would expect As-deficient growth conditions...
at the nanowire–particle interface. One possible scenario is that additional arsenic can reach the growth zone via an As vacancy diffusion mechanism through the GaAs nanowire. Moreover, under As-deficient conditions, one would also expect that As vacancies could be left behind within the GaAs nanowire by the advancing interfacial growth zone. A subsequent annealing process in arsenic vapor might be helpful to remove these vacancies. Therefore, it is important to understand \( V_{\text{As}} \) diffusion within GaAs bulk, in order to comprehensively understand the As supply path during the growth process and to estimate a suitable annealing temperature for removing \( V_{\text{As}} \) in a nanowire. A previous theoretical study based on density functional theory (DFT) \(^{23,25}\) calculated relatively high migration barriers of \( \sim 2.4 \text{ eV} \) for a \( V_{\text{As}} \) in a zincblende GaAs. \(^{25}\) This seemingly implies that As transport through the nanowire could be inefficient. However, the convergence of the atomic-orbital basis sets employed in these DFT calculations has not been demonstrated.

While wurtzite GaAs cannot be obtained in bulk form by ordinary growth techniques, the GaAs nanowires grown with Au catalyst may exhibit both zincblende (ZB) and wurtzite (WZ) structures, or alternating segments of these (and other) polytypes through stacking faults. \(^{12,27,29}\) Hence, it is crucial to understand \( V_{\text{As}} \), \( \text{Ga}_{\text{As}} \), and Au defects in both ZB and WZ GaAs crystals. There is considerable knowledge, both from experimental \(^{25}\) and theoretical \(^{10,31}\) sides, about intrinsic point defects in ZB GaAs. However, experimental data on point defects in WZ GaAs is still elusive. In this work, we will perform plane-wave DFT calculations to study various properties associated with \( V_{\text{As}} \), \( \text{Ga}_{\text{As}} \), and Au defects in ZB and WZ GaAs crystals, and to investigate and compare \( V_{\text{As}} \) diffusion in both GaAs polytypes. This paper is organized as follows: The computational approach and supercell models are described in Sec. II. The formation energies of \( V_{\text{As}} \), \( \text{Ga}_{\text{As}} \) defects and Au impurities in ZB and WZ GaAs crystals are discussed in Sec. III. The diffusion of \( V_{\text{As}} \) in various charge states in ZB and WZ GaAs crystals are presented in Sec. IV. We summarize our work in Sec. V.

II. METHODS OF CALCULATION

In this work, we have performed DFT calculations to study \( V_{\text{As}} \), \( \text{Ga}_{\text{As}} \), and substitutional Au impurities in ZB and WZ GaAs using the supercell method. The conventional unit cell for a ZB and a WZ GaAs crystal is shown in (a) and (b), respectively. The As and Ga atoms are represented by large pink and small green spheres, respectively.

![FIG. 1: (Color online) The structure of ZB and WZ GaAs crystals. The conventional unit cell for a ZB and a WZ GaAs crystal is shown in (a) and (b), respectively. The As and Ga atoms are represented by large pink and small green spheres, respectively.](image-url)
that are computed to be 1.15 eV and 0.99 eV in ZB and WZ GaAs, respectively, are much closer to experimental values. Moreover, we conclude from these calculations that the valence band maximum experiences a down-shift of 0.48 eV in ZB GaAs (0.36 eV in WZ GaAs). These values are in good agreement with recent literature\textsuperscript{22} and will be used as corrections when our computed results are compared to experiment. The orthorhombic Ga (space group Cmca) crystal and trigonal As (space group R3m) crystal are used to compute the Ga and As chemical potentials.

Since ZB and WZ segments co-exist in GaAs nanowires, the band edges from ZB and WZ supercell calculations should be aligned accordingly. We have constructed a 50 atom supercell of a heterostructure of WZ and ZB GaAs. The supercell consists of 13 ZB and 12 WZ bilayers that stack along [111] or [0001] for a ZB or a WZ segment, respectively. The constructed heterostructure is optimized for both the lattice constant and internal coordinates. Note that the lateral dimension of the heterostructure happens to coincide with the average of the WZ and ZB lattice parameters. The valence band offset of the ZB and WZ segments can be computed\textsuperscript{23} as

\[
\Delta E_{VB}(\text{GaAs}) = E_{VB}^{ZB} - E_{VB}^{WZ} - (E_{core}^{ZB}(\text{As}) - E_{core}^{WZ}(\text{As})) + (E_{core}^{ZB}(\text{As}) - E_{core}^{WZ}(\text{As})),
\]

where \(E_{VB}^{ZB}\) and \(E_{VB}^{WZ}\) are the valence band top energies at the \(\Gamma\)-point for ZB and WZ GaAs, respectively, \(E_{core}^{ZB}(\text{As})\) and \(E_{core}^{WZ}(\text{As})\) are the core level energies of As atoms in bulk ZB and WZ GaAs, respectively, \(E_{core}^{ZB}\) and \(E_{core}^{WZ}\) are the core level energies of As atoms in ZB and WZ segments of the heterostructure, respectively. We compute the band offset to be \(\Delta E_{VB}(\text{GaAs}) = -0.0601\) eV, in good agreement with the value of \(-0.0632\) eV from a previous calculation\textsuperscript{23}

III. THE ENERGETICS OF DEFECTS AND Au IMPURITIES IN GaAs NANOWIRES

We start by calculating the formation energies of relevant intrinsic defects. The formation energy of a \(q\)-charged \((q\) is an integer number) defect (or impurity) \(X\) at site \(Y\) as a function of the Fermi level \(\varepsilon_F\) is defined by

\[
E_f[X^q_Y; \varepsilon_F] = E[X^q_Y] - E_{host} - \sum_i n_i \mu_i + q(\varepsilon_F + E_v) + E_{corr}.
\]

Here, \(E[X^q_Y]\) is the total energy of a \(q\)-charged supercell with a defect \(X_Y\) and \(E_{host}\) is the energy of a perfect GaAs bulk supercell with the same shape. \(n_i\) and \(\mu_i\) represent the change in the number of species \(i\) in the supercell and the chemical potential for a species \(i\), respectively. \(\varepsilon_F\) is the Fermi level that depends on the doping condition, and \(E_v\) is the valence band top energy of the corresponding bulk GaAs crystal. Due to the \((2\times2\times2)\) \(k\)-point mesh used for supercell calculations, the gap between the highest occupied (HOMO) and the lowest unoccupied (LUMO) orbitals is much higher in these supercell calculations compared to the gap at the \(\Gamma\)-point in GaAs bulk calculations. Even though this widened gap is a technical artifact of our method, it puts us in position to vary \(\varepsilon_F\) in a rather wide range while still maintaining the physically correct charge distribution localized near the defect. The energy interval around \(E_v\) in which our calculations can be expected to yield physically meaningful charge transfer levels, as a charged defect cannot transfer charge to the LUMO or from the HOMO, is indicated in the figures. The linear and quadratic correction term with respect to \(q\) of \(E_{corr} = \Delta V q + \alpha q^2 / 2L\) accounts for the spurious electrostatic interaction between periodic images of charged defect.\textsuperscript{24,25} \(\Delta V\) is a correction for the spurious potential off-set induced by the finite defect concentration in the calculation; it is calculated from the energy difference of atomic core levels between a neutral supercell with an \(X_Y\) defect and a perfect bulk

![FIG. 2: (Color online) The formation energy of an As vacancy (a) and a Ga antisite (b) in various charge states in GaAs polytypes at different doping conditions, as a function of the Fermi level \(\varepsilon_F\). The formation energies of As vacancies in ZB GaAs and WZ GaAs are shown as dashed and solid lines, respectively. The thick lines represent stable charge states. The vertical lines indicate the HOMO and LUMO levels in the defect-free supercell and thus delimit the energy interval where the GGA total energies are considered reliable. The left and right y-axes show the formation energies under As-rich (\(\mu_{As}^{upper}\)) and Ga-rich (\(\mu_{As}^{lower}\)) conditions as described in the text. Here, one has the identity \(\mu_{As}^{lower} = \mu_{As}^{upper} - 0.7\) eV.](image)
supercell. The values for $\alpha$ and $\epsilon$, the Madelung constant and the static dielectric constant, respectively, are taken according to the ZB or WZ polytype of bulk GaAs, and $L$ is the supercell dimension used in the corresponding calculations. The values of $\alpha$, $\epsilon$, and $L$ are listed in Table I in the Appendix for the cases of ZB and WZ GaAs crystals, respectively. Our computed dielectric constant $\epsilon$ for ZB GaAs is 32% larger than the experimental value of 0.90 e\text{A}^{-1}V^{-1}. At the growth condition, the chemical potentials of Ga and As are in equilibrium with bulk GaAs. Thus, one has the identity $\mu_{\text{Ga}} + \mu_{\text{As}} = \mu_{\text{GaAs}}$, where $\mu_{\text{GaAs}} = -E_{\text{GaAs}}^{bulk}$ is the cohesive energy per formula unit of a pertinent GaAs polytype. The range of the As chemical potential is specified in accordance with the growth condition, with the upper bound set to be at the equilibrium with bulk As, i.e., $\mu_{\text{As}}^{\text{upper}} = -E_{\text{As}}^{\text{bulk}}$. The lower bound is set to be at the equilibrium with bulk Ga as $\mu_{\text{As}}^{\text{lower}} = -E_{\text{Ga}}^{\text{bulk}}$. Disregarding the difference of the cohesive energies of GaAs of 20 meV in ZB and WZ crystals, we align the upper bound $\mu_{\text{As}}^{\text{upper}}$ for ZB and WZ to the same value. We take the lower bound $\mu_{\text{As}}^{\text{lower}}$ to be 0.7 eV below $\mu_{\text{As}}^{\text{upper}}$, so that $\mu_{\text{As}}^{\text{lower}}$ is very close to a Ga-rich condition for both ZB and WZ GaAs crystals. The bulk energies of GaAs, Ga and As crystals are calculated using the optimized lattice parameters. Note that the upper and lower bounds of the As chemical potentials correspond to As- and Ga-rich growth conditions, respectively. In addition, the cohesive energy bulk Au per atom is inserted for the Au chemical potential, i.e., $\mu_{\text{Au}}$ respectively. In addition, the cohesive energy bulk Au per atom is inserted for the Au chemical potential, i.e., $\mu_{\text{Au}}$ respectively. The bulk energies of GaAs, Ga and As crystals are calculated using the optimized lattice parameters. Note that the upper and lower bounds of the As chemical potentials correspond to As- and Ga-rich growth conditions, respectively. In addition, the cohesive energy bulk Au per atom is inserted for the Au chemical potential, i.e., $\mu_{\text{Au}}$ respectively.

The bulk GaAs is indeed a physical feature or not should be determined by future experiments.

The Ga antisite $\text{Ga}_{\text{As}}$ could be another intrinsic defect within a growing GaAs nanowire under As-deficient conditions, and we show the formation energies of $\text{Ga}_{\text{As}}$ as a function of $E_{\text{F}}$ in Fig. 2(b). The formation energies are computed using Eq. 2 with the potential off-set $\Delta V$ associated with $\text{Ga}_{\text{As}}$ defects listed in Table IV in the Appendix. The formation energies are specified for both Ga-rich (right $y$-axis in Fig. 2(b)) and As-rich (left $y$-axis Fig. 2(b)) conditions, and formation energies are 1.4 eV lower in a Ga-rich condition than in an As-rich condition. In both ZB and WZ GaAs crystals, $\text{Ga}_{\text{As}}$ has charge states from $2^+$ to $2^-$ may be stable under certain doping conditions. The associated formation energies in WZ GaAs are overall lower than in ZB GaAs. The $\text{Ga}_{\text{As}}^0$ and $\text{Ga}_{\text{As}}^{+}$ defects are energetically more favorable by 0.13-0.14 eV in WZ than in ZB, whereas a $\text{Ga}_{\text{As}}$ defect is only 0.01 eV more stable in WZ. As a result, the charge transfer levels (0/−) differ by 0.12 eV in ZB and WZ. It follows that, on an absolute scale, the charge transfer levels are located at $E_{\text{F}}^{\text{ZB}}+0.21$ and 0.33 eV in ZB and WZ segments of a GaAs nanowire, respectively. We notice that both intrinsic defects of $\text{V}_{\text{As}}$ and $\text{Ga}_{\text{As}}^+$ have deep charge transfer levels and they are deeper in WZ GaAs. Comparing Fig. 2(a) and (b), one may find that $\text{V}_{\text{As}}$ are more stable than $\text{Ga}_{\text{As}}$ for the doping conditions of $E_{\text{F}} - E^{\text{ZB}}_{\text{v}} < 0.21$ (0.27) eV in ZB (WZ) under As rich conditions, while $\text{Ga}_{\text{As}}$ are more stable than $\text{V}_{\text{As}}$ for the doping conditions of $E_{\text{F}} - E^{\text{ZB}}_{\text{v}} > 0.21$ (0.27) eV in ZB (WZ). When comparing to experiment, one should take into account that the “true” valence band top is lower than the $E_{\text{v}}$ resulting from our DFT-GGA calculations, such that the range of horizontal-axis values plotted in Fig. 2 approximately reflects the “true” band gap.
FIG. 3: (Color online) The formation energies of a substitutional Au defect in the ±1-charged, ±2-charged, and neutral states in WZ and ZB GaAs crystals. The formation energies of a substitutional Au impurity for a lattice As atom and a lattice Ga atom are shown in (a) and (b), respectively. The formation energies of Au impurities in ZB GaAs and WZ GaAs are shown as dashed and solid lines, respectively. The thick lines represent stable charge states. The vertical lines indicate the HOMO and LUMO levels in the defect-free supercell, same as Fig. 2. The left and right y-axes show the formation energies under As-rich ($\mu_{As}^{upper}$) and Ga-rich ($\mu_{Ga}^{lower}$) conditions as described in the text.

We also study the energetics of substitutional Au impurities in GaAs crystals, and the computed formation energies of $\text{Au}_{\text{As}}$ and $\text{Au}_{\text{Ga}}$ as a function of $\varepsilon_F$ are shown in Fig. 3. The formation energies of $\text{Au}_{\text{As}}$ and $\text{Au}_{\text{Ga}}$ are computed using Eq. 2 with the potential offsets associated with $\text{Au}_{\text{As}}$ and $\text{Au}_{\text{Ga}}$ listed in Table IV in the Appendix. Moreover, the formation energies are specified for both Ga-rich (right y-axis in Fig. 3) and As-rich (left y-axis Fig. 3) conditions. It is found that under an As-rich growth condition an $\text{Au}_{\text{Ga}}$ is energetically more favorable than an $\text{Au}_{\text{As}}$ by about one to two eV both in ZB GaAs and in WZ GaAs, depending on the doping conditions. However, under a Ga-rich growth condition, the formation energy of an $\text{Au}_{\text{Ga}}$ is 0.7 eV higher than that under an As-rich condition, while the formation energy of an $\text{Au}_{\text{As}}$ becomes 0.7 eV lower. Therefore, under a Ga-rich condition, the $\text{Au}_{\text{As}}$ defects turn out to be more stable than $\text{Au}_{\text{Ga}}$. We expect that $\text{Au}_{\text{Ga}}$ defects with charge states from 2+ to 2− may be stable under certain doping conditions. An $\text{Au}_{\text{Ga}}$ has its charge transfer levels mostly in the lower part of the band gap, while the charge transfer levels of an $\text{Au}_{\text{As}}$ lie at somewhat higher energies. The $\text{Au}_{\text{As}}$ impurities occur preferentially as 2+, + or neutral defects, while the levels of negatively charged defects lie probably already above the conduction band minimum of the host material. Figure 3(a) indicates the charge transfer levels of $\text{Au}_{\text{As}}$ are deep, $E_v^{\text{ZB}} + 0.78$ eV and $E_v^{\text{ZB}} + 0.91$ eV for ZB and WZ crystals, respectively. In contrast, an $\text{Au}_{\text{Ga}}$ impurity switches from a neutral state to a 1− charged state at $E_v^{\text{ZB}} + 0.22$ eV and $E_v^{\text{ZB}} + 0.35$ eV in ZB and WZ crystals, respectively, as seen in Fig. 3(b). As stated before, one should allow for a correction of about 0.4 eV to our $E_v$ value when comparing to experiment. Experimental studies using deep-level transient spectroscopy and photoluminescence spectroscopy have identified an Au-related deep acceptor level of about 0.4 eV above the valence band in bulk GaAs. Moreover, we find an $\text{Au}_{\text{Ga}}$ has a lower formation energy compared to an $\text{Au}_{\text{As}}$ under the moderately As-rich growth conditions conventionally used. Taking into account the down-shift of $E_v$ with respect to the DFT-GGA value (see e.g., Ref. 44), it is plausible that the experimentally observed defect level at 0.4 eV above the valence band is indeed due to $\text{Au}_{\text{Ga}}$ defects.

We conclude this Section by discussing the energetics of defects caused by a deficiency of arsenic under varying growth conditions. In Fig. 3(a), we compare the formation energies of the lowest energy $V_{\text{As}}$, $\text{Au}_{\text{As}}$ and $\text{Ga}_{\text{As}}$ defects in p-type ZB and WZ GaAs crystals with the condition of $\varepsilon_F = E_v^{\text{ZB}} = 0$, as a function of As chemical potential $\mu_{\text{As}}$. Our calculations show that $\text{Au}_{\text{As}}$ impurities have the lowest formation energies, while $V_{\text{As}}$ and $\text{Ga}_{\text{As}}$ defects have clearly higher formation energies. Figure 3(b) shows the same comparison for n-type ZB and WZ GaAs crystals with $\varepsilon_F = E_v^{\text{ZB}} + 1.0$ eV. Here, a $\text{Ga}_{\text{As}}$ in the 2− charge state has the lowest formation energy, followed by $\text{Au}_{\text{As}}$ and $V_{\text{As}}$. Consequently, when growing GaAs nanowires with a gold catalyst droplet, some $\text{Au}_{\text{As}}$ defects will be formed in the GaAs nanowire, in particular for a p-doped material. The Au impurities act as deep centers and are thus detrimental to the optical properties of nanowires. In gold-free self-catalyzed growth, $\text{Ga}_{\text{As}}$ and $V_{\text{As}}$ defects may exist in the nanowire, albeit at much smaller concentration than the Au defects if the material is p-doped. Out of these three defect species, only the $V_{\text{As}}$ defect is expected to be mobile via a hopping diffusion mechanism. The mobility of the $\text{Ga}_{\text{As}}$ and $\text{Au}_{\text{As}}$ defects will most probably be vacancy-mediated, and thus require the $V_{\text{As}}$ presence. Moreover, it is conceivable that $V_{\text{As}}$ hopping diffusion could play a role in the nanowire growth process as a mechanism supplying arsenic to the interfacial growth zone between the nanowire tip and the catalyst droplet. Hence, we will investigate the detailed diffusion processes of $V_{\text{As}}$ in GaAs crystals in the following Section.
As VACANCY DIFFUSION IN GaAs

Arsenic vacancies in GaAs have been characterized experimentally by positron annihilation\[^{[22]}\] and by scanning-tunneling microscopy\[^{[13]}\]. For ZB GaAs, a number of theoretical studies, using (semi-)local DFT\[^{[19,20]}\] or hybrid functionals\[^{[14,21]}\], have been carried out, and the diffusion pathway of the arsenic vacancy has been investigated\[^{[28]}\]. Interestingly, these calculations claimed the existence of a metastable interstitial state along the diffusion path in ZB GaAs, while this issue is unresolved for WZ GaAs.

We start by characterizing the geometry of $V_{As}$ in GaAs crystals in more detail. As shown in Fig. 5, the neighboring Ga atoms with respect to a $V_{As}$ define a Ga tetrahedron. To specify the local deformation of a crystal due to the $V_{As}$ presence, we study the relaxation of the edge length $l$ of the tetrahedron and compare it to the equilibrium distance between two neighboring Ga atoms in the ZB (WZ) GaAs crystal of $l_0 = 4.07$ (4.05) Å. Similarly, the relaxed tetrahedron volume $V$ will be compared to the equilibrium tetrahedron volume in ZB (WZ) GaAs crystal of $V_0 = 7.97$ (7.93) Å$^3$.

For a $V_{As}$ in ZB GaAs, the edge lengths of the Ga atom tetrahedron are all contracted (see the right panel of Fig. 5(a)), resulting in a significantly reduced volume of $V = 0.516V_0$ (48.4% compression) as listed in Table 1. Especially, the A-D and B-C edges are most contracted up to $l = 0.702l_0$ (29.8% compression), while other edges

![Diagram](image)

**FIG. 4:** (Color online) The formation energies of $V_{As}$, $Au_{As}$ and $Ga_{As}$ defects in GaAs crystals as a function of $\mu_{As}$. In (a) and (b), the Fermi energy is set to be at the calculated top of valence band and 1 eV above, respectively, to describe a p-type or an n-type material. Only the energetically most favorable charge states are shown.

**FIG. 5:** (Color online) The geometry of $V_{As}$ in GaAs crystals. The relaxations of $V_{As}^+$ and $V_{As}^-$ in ZB GaAs are illustrated in (a), while the relaxations of two sets of stable $V_{As}^+$ and $V_{As}^-$ in WZ GaAs are characterized in (b) and (c), respectively. We have found two stable $V_{As}^+$ (M1 and M2) and two $V_{As}^-$ (M1 and M2) in WZ GaAs. A $V_{As}$ is highlighted by a big blue sphere, and its four neighboring Ga atoms are highlighted by A, B, C, and D labeled spheres. These neighboring Ga atoms form a tetrahedron. The other attached As and Ga atoms are represented by small pink red and large green spheres, respectively. The right panel indicates the relaxed edge length of the Ga tetrahedron. The upper and lower numbers refer to a $V_{As}^+$ and a $V_{As}^-$, respectively.

**TABLE I:** Ga tetrahedron volumes of $V_{As}$ in various charge states. $V_0$ represents the equilibrium tetrahedron volume in a ZB (WZ) GaAs crystal of $V_0 = 7.97$ (7.93) Å$^3$.
are compressed by $\sim 11\%$. The deformation reduces the symmetry of the distorted Ga tetrahedron to $D_{2d}$ which is in accordance with previous studies. In WZ GaAs, there exist two different, but energetically very similar structures (M1 and M2) for a relaxed $V_{As}^-$ (see Fig. 5(b) and (c)). The WZ-M2 configuration is slightly more stable than the WZ-M1 configuration in terms of energetics. Both WZ-M1 and WZ-M2 $V_{As}^-$ configurations exhibit similar deformations as a $V_{As}^-$ in ZB, and the relaxed tetrahedron volumes are reduced by 48.4 \% to 48.8 \%, respectively. This is comparable to the ZB case. The relaxed Ga tetrahedron for WZ-M1 and WZ-M2 $V_{As}^-$ possesses a $C_{2v}$ and a $C_1$ symmetry, respectively.

For a $V_{As}^+$, the tetrahedron of neighboring Ga atoms contracts in volume by only 7.8 \% in WZ GaAs, whereas it contracts by 7.4 \% to 11.4 \% in WZ GaAs, as listed in Table I. In particular, $V_{As}^+$'s have one edge compressed, while the other edges are slightly expanded. The WZ-M2 $V_{As}^+$ configuration has the A-C edge (within the $ab$ plane) compressed. In contrast, the WZ-M1 $V_{As}^+$ configuration has the A-D edge (out of the $ab$ plane) compressed. In other words, the deformation of $V_{As}^+$ in WZ GaAs is anisotropic, and hence the relaxed Ga tetrahedron for WZ-M1 and WZ-M2 $V_{As}^+$ possesses $C_{2v}$ or $C_1$ symmetry, respectively. In addition, despite the neutral state being unstable, we mention that the volumes of neutral As vacancies are 0.757$V_0$ in ZB and 0.696$V_0$ in WZ-M1, respectively. It is worth noting that the vacancy volume becomes smaller with increasing electronic charge. The physical reason for this general trend lies in the fact that the additional electrons in the vacancy allow for the filling of orbitals with bonding character that are formed by symmetry-adapted linear combinations of the Ga dangling-bond orbitals.

In the following, we assume that the $V_{As}$ diffusion proceeds via a neighboring As atom of the arsenic sublattice hopping into the vacancy. Schematically, an As atom hops out of an initial Ga-tetrahedron cage into an adjacent target Ga-tetrahedron cage that previously enclosed the As vacancy site. We refer to the tetrahedron that surrounds the migrating As atom as the initial tetrahedron, and refer to the adjacent Ga-tetrahedron that surrounds the target As vacancy site as the target tetrahedron. We note that the reverse process occurs with the same probability, with the role of initial and target tetrahedron interchanged. The diffusion process can be decomposed into an As escape from the initial tetrahedron, its interstitial motion between the two tetrahedra, and an entry into the target tetrahedron. Note that one of the Ga atoms is located at the common apex of both tetrahedra.

Since ZB GaAs is a cubic crystal, the four possible diffusion paths of a $V_{As}$ to four neighboring As sites are symmetrically equivalent. The diffusion path shown Fig. 6 is sufficient to describe As diffusion in ZB GaAs. Figure 6(a) illustrates the detailed diffusion process of a $V_{As}^+$ in ZB GaAs, indicating an overall migration barrier of 1.93 eV. The local minimum configurations ($i$ and $v$ in Fig. 6(a)) as well as the saddle point configurations ($ii$ and $iv$ in Fig. 6(a)) along the diffusion path are illustrated by the ball-and-stick models in the figure. In the target tetrahedron, the AG edge corresponds to the short edge (the AD in Fig. 5(a)). By expanding the bond between As and Ga at the D-site, the diffusing As atom escapes from the initial tetrahedron. During the escape process, the initial tetrahedron is expanding, while the target tetrahedron is contracting. After passing through the ABC face of the tetrahedron, the diffusing As atom arrives at the first saddle point ($ii$) which represents the transition state for $V_{As}^+$ migration. In this configuration, the As-Ga bonds to the initial tetrahedron apexes are broken except for the A-site. The target tetrahedron volume is compressed from 0.922$V_0$ to 0.719$V_0$ which corresponds to the volume of a neutral As vacancy (see Table I). This observation implies that a positively charged...
As vacancy in the target tetrahedron attracts electrons ahead of the As migration. When migrating toward the target tetrahedron in the interstitial space, the diffusing As atom reaches an interstitial state (iii) with a shallow energy dip. At this moment, the diffusing As atom is located at an octahedral interstitial site in ZB GaAs. In this interstitial state, the migrating As creates two additional bonds to target tetrahedron apexes, indicating that the As atom starts to supply electrons to the target tetrahedron. Consequently, the target tetrahedron volume further contracts to 0.662\(V_0\). This volume is still a bit larger than for a negatively charged As vacancy, but notably smaller than for a neutral As vacancy. Passing through the AEF face of the target tetrahedron, the diffusing As atom enters the target vacancy. The diffusion process is thus completed. When the As atom diffuses into the target tetrahedron, it establishes the As-Ga bond.

Figure 6(b) shows the \(V_{As}^-\) diffusion path in ZB GaAs, which is similar to \(V_{As}^+\) diffusion with a slightly lower migration barrier of 1.91 eV. Again, we find the escape barrier from the initial tetrahedron to be the rate-limiting step. In the interstitial space, there is also an interstitial As configuration located in a shallow dip, and it occupies an octahedral interstitial site in ZB GaAs. The associated initial and target tetrahedra at this stage have volumes of 1.102\(V_0\) and 0.673\(V_0\), respectively. We note that the tetrahedron volume expands while loosing an electron (see Table 1). The diffusing As atom at the interstitial site has to overcome an entry barrier of 0.13 eV to migrate into the target tetrahedron, which is 0.19 eV lower than that of the reverse diffusion process. The initial tetrahedron volume is reduced to the \(V_{As}^-\) value after the diffusing As passes through the second saddle point. We note that the two saddle points along the diffusion path have different energies. Although an oversimplified consideration solely based on the atomic positions suggests that a symmetric mechanism might exist, the observed symmetry breaking is physical because the charge balance between the two tetrahedra under the presence of the migrating As atom is non-symmetric. Therefore, it is meaningful to distinguish between the escape (first) saddle point or the entry (second) saddle point to be rate-limiting.

Our results qualitatively agree with the previous theoretical study which reported migration barriers of 2.41 eV and 2.38 eV for \(V_{As}^+\) and \(V_{As}^-\) diffusion in ZB GaAs, respectively, using atomic orbital basis sets. Both in their and in our work, the computed diffusion barrier of a \(V_{As}^-\) is slightly lower than that of a \(V_{As}^+\). However, in our plane-wave-based calculations, diffusion barriers of \(V_{As}^+\) and \(V_{As}^-\) are computed to be 1.93 eV and 1.91 eV, respectively, which are about 0.5 eV lower in energy than the values reported in Ref. 26. We believe that these differences are due to the more complete basis set for the wave functions in our calculations, which allows for a more accurate description of the energetics, in particular at transition state geometries.

Next, we perform analogous calculations for \(V_{As}^+\) and \(V_{As}^-\) diffusion in WZ GaAs. Due to the lower crystal symmetry of WZ, one needs to consider two pathways; i.e., an As vacancy can diffuse within the ab plane by hopping from site 1 to site 2 or along the c axis by hopping from site 2 to site 3, as illustrated in Fig. 7(b). First, we discuss the vacancy diffusion within the ab plane. Figure 7 shows that \(V_{As}^+\) and \(V_{As}^-\) can diffuse in the ab plane in WZ GaAs with migration barriers of 1.79 eV and 1.60 eV, respectively. As discussed above, there are two different minimum configurations for \(V_{As}^+\) and \(V_{As}^-\) defects, M1 and M2, in WZ GaAs. The transition from the more
stable M2 to the M1 configuration costs relatively low activation energies, 0.11 eV for a V\textsubscript{As}\textsuperscript{+} and 0.17 eV for a V\textsubscript{As}\textsuperscript{−}. We basically find similar diffusion processes as in ZB GaAs, i.e., an As escape from the initial tetrahedron, an As motion within the interstitial space, and an As entry into the target tetrahedron. In the intermediate configuration in the \textit{ab} plane, the As atom is located in an octahedral interstitial site in WZ GaAs. Thus, the local symmetry of the intermediate is the same for WZ and ZB along this path. However, the overall migration barriers are up to 0.2-0.3 eV lower in WZ than in ZB. In the V\textsubscript{As} diffusion, we note that the volume contraction of the initial tetrahedron takes place earlier than in the other cases (see Fig. 8(b)), i.e., its volume is reduced to 0.69\textit{V}\textsubscript{0} when As reaches the interstitial configuration. In comparison, for V\textsubscript{As}\textsuperscript{+} diffusion in ZB GaAs, the initial tetrahedron has a volume of 1.102\textit{V}\textsubscript{0} when the diffusing As is at the interstitial site. Moreover, for V\textsubscript{As}\textsuperscript{−} s in WZ and ZB crystals, the associated initial tetrahedron volume is about 1.8\textit{V}\textsubscript{0} to 1.9\textit{V}\textsubscript{0} when the diffusing As is at the interstitial site. This early compression of the initial tetrahedron for the V\textsubscript{As}\textsuperscript{−} diffusion also results in a compressed interstitial space. In the interstitial space, the diffusing As atom forms three bonds to the target tetrahedron and one bond to the initial tetrahedron. Hence, the interstitial V\textsubscript{As}\textsuperscript{−} is fully coordinated. This could explain the low migration barrier of 1.60 eV associated with the V\textsubscript{As} diffusion within the \textit{ab} plane in WZ GaAs.

Secondly, we discuss the V\textsubscript{As} diffusion along the \textit{c}-axis in WZ GaAs. Figure 8 shows that V\textsubscript{As}\textsuperscript{−} and V\textsubscript{As}\textsuperscript{+} defects can diffuse along the \textit{c}-axis with relatively high migration barriers of 2.44 eV and 2.07 eV, respectively. Again, the diffusion process consists of the three steps introduced above: The diffusing As atom escapes from the initial tetrahedron cage through the ABC face. It enters the neighboring octahedral interstitial area through the ABF face and finally hops into the target tetrahedron through the AFG face. When the diffusing As passes the ABF face, it almost crosses the AF edge. This may result in the high migration barriers associated with the \textit{c}-axis diffusion in WZ GaAs. For the V\textsubscript{As}\textsuperscript{−} diffusion, there exists a stable interstitial configuration (iii) as shown in Fig. 8(b). For this configuration, the diffusing As atom is located at a tetrahedral interstitial site. It is fully coordinated and its energy is only 1.03 eV above the ground state \textit{i} configuration. This may result in the lower V\textsubscript{As}\textsuperscript{−} migration barrier of 2.07 eV compared to the V\textsubscript{As}\textsuperscript{+} diffusion as shown in Fig. 8.

Finally, we discuss the possibility of reducing the concentration of V\textsubscript{As} defects in nanowires by annealing under an arsenic atmosphere. We use the migration barrier of 1.93 eV of a V\textsubscript{As}\textsuperscript{+} in ZB GaAs to estimate the required annealing time. The diffusivity associated with the V\textsubscript{As} can be estimated as

\[ D \approx \frac{z^2\nu_0}{\nu_0} \exp \left(-\frac{\Delta E}{k_B T}\right), \]

where \nu_0 = 10^{13} s\textsuperscript{-1} is the estimated attempt frequency, \textit{k}_B is the Boltzmann constant, the annealing temperature is set to be \textit{T} = 700 K, \Delta E is the migration energy of an arsenic vacancy in GaAs, and \textit{a}_0 is the distance between two neighboring As atoms in a GaAs crystal and is also the hop distance for V\textsubscript{As} diffusion. In a nanowire growing along the [\textit{111}] direction, V\textsubscript{As}s are expected to diffuse to the side wall. Using a typical radius of a GaAs nanowire, \textit{R} = 20 nm (Ref. 7), the annealing time required to remove the V\textsubscript{As}s can be computed as \textit{t} = \textit{R}^2/\textit{D} = 5.26

| TABLE II: Diffusion constants for V\textsubscript{As} diffusion in ZB and WZ GaAs at \textit{T} = 700 K. All numbers are given in units of \textit{cm}\textsuperscript{2}/s. The V\textsubscript{As} diffusivity along the \textit{c} direction in WZ GaAs is the lowest. |
|-----------------|-----------------|-----------------|
|                 | ZB              | WZ-\textit{ab}  | WZ-\textit{c}  |
| V\textsubscript{As}\textsuperscript{+} | 2.11 \times 10^{-19} | 2.13 \times 10^{-19} | 4.46 \times 10^{-20} |
| V\textsubscript{As}\textsuperscript{−} | 2.94 \times 10^{-19} | 4.97 \times 10^{-19} | 2.05 \times 10^{-17} |

FIG. 8: (Color online) The energy path of V\textsubscript{As}\textsuperscript{+} (a) and V\textsubscript{As}\textsuperscript{−} (b) diffusion along the \textit{c}-axis of in WZ GaAs. The structures of various stages (i – v) are illustrated. The color scheme is the same as in Fig. 6.
hours. In WZ GaAs, the reduction of the energy barrier by 0.14 eV to 1.79 eV reduces the annealing time by a factor of 10 to 31.3 minutes. Thus, we conclude that the $V_{A\text{s}}$ introduced in a GaAs nanowire during As-deficient growth can be annealed within a reasonable time frame at a temperature of 700 K. We hereby summarize the diffusivities of $V_{A\text{s}}^+$ and $V_{A\text{s}}^-$ defects in ZB and WZ GaAs crystals for various diffusion processes in Table III.

V. DISCUSSION AND SUMMARY

Using DFT calculations, we have characterized the $V_{A\text{s}}$, Ga$_{\text{As}}$, and Au defects in GaAs crystals that may be introduced in GaAs nanowires grown with the help of metal droplets under As-deficient conditions at the interfacial growth zone. The substitutional Ga$_{\text{As}}$, Au$_{\text{As}}$, and Au$_{\text{Ga}}$ defects exhibit similar formation energies and defect levels in both ZB and WZ GaAs crystals. Moreover, a $V_{A\text{s}}$ defect behaves as a ‘negative $U$’-system, switching from a $V_{A\text{s}}^+$ in a $p$-doped material to a $V_{A\text{s}}^-$ in an $n$-doped material, for both GaAs crystals. In case that a Au droplet is used a catalyst for nanowire growth, the formation of substitutional Au defects is possible and is found to be energetically more favorable than the formation of Ga$_{\text{As}}$ or $V_{A\text{s}}$ defects. Moreover, we have shown that it is energetically more favorable by about 1 to 2 eV for an Au substitutional defect to replace a lattice Ga atom than a lattice As atom in either ZB or WZ GaAs. Given that DFT-GGA calculations give a too small band gap, the calculated acceptor level of Au$_{\text{Ga}}$ at $E_v$ + 0.22 eV is found to be in reasonable agreement with the experimental value of $E_v$ + 0.4 eV in ZB GaAs.

In Au-free, self-catalyzed growth of nanowires that are grown at higher temperatures, the formation of Ga$_{\text{As}}$ could be expected. In particular, for Ga-rich growth conditions and $n$-type material, the Ga$_{\text{As}}^2$ species has a low formation energy. This could lead to growth of non-stoichiometric, Ga-enriched GaAs. The incorporation of Ga$_{\text{As}}^2$ will counteract the $n$-doping by deliberately added donor species. This may explain why it is rather difficult to obtain $n$-type conductivity in ZB GaAs nanowires, and only high concentrations of Sn$_{\text{Ga}}$ have proven successful so far. Under less Ga-rich growth conditions, the formation of $V_{A\text{s}}$ could be expected, and their diffusion might even play a role for the material transport in the growth of a GaAs nanowire. We note that As interstitials, which could in principle also contribute to As mass transport, tend to have a higher formation energy than $V_{A\text{s}}$, apart from very As-rich conditions. Since we are interested in the As-deficient growth conditions below the nanoparticle, we don’t consider the As interstitial diffusion here. Our results show that i) $V_{A\text{s}}$ can diffuse within ZB GaAs with a migration barrier of about 1.9 eV; and ii) $V_{A\text{s}}$ diffuse favorably within the $ab$ plane in WZ GaAs with somewhat lower migration barriers of 1.6 to 1.8 eV. Based on these results, we estimate that it takes about five hours to anneal the $V_{A\text{s}}$ at 700 K in a ZB GaAs nanowire, but only 30 minutes in a WZ nanowire. Thus, an annealing of GaAs nanowires under an arsenic atmosphere could be useful to obtain samples with a longer lifetime for the charge carriers. However, the diffusivity of $V_{A\text{s}}$ in the nanowires is too low to contribute substantially to the arsenic supply at the nanowire growth zone, in particular in WZ GaAs, where the diffusion barrier along the $c$-axis is higher than in ZB GaAs.

Acknowledgments

We acknowledge Center for Computational Sciences and Simulation (CCSS) of University Duisburg-Essen for the computer time and the Deutsche Forschungsgemeinschaft DFG for the financial support through the project KR 2057/5-1.

Appendix: Parameters for computing formation energies

The Madelung constants, the calculated dielectric constants, and the dimensions of ZB and WZ GaAs crystals are listed in Table III. $L$ represents the distance between the nearest neighbor defects within a supercell. It is taken to be length of the $a$-axis of a 216 atom ZB and a 96 atom WZ GaAs crystal as listed in Table III. The dielectric constants are the $\epsilon_{aa}$ components of pertinent dielectric tensors. They include both electronic and ionic contributions. The values of the potential off-set corrections for various defect and impurity calculations are listed in Table IV.
C. Gutsche, A. Lysov, I. Regolin, K. Blekker, W. Prost, and F.-J. Tegude, Nanoscale Res. Lett. 6, 65 (2011).