

Magic Number Vacancy Aggregates in GaAs: Structure and Positron Lifetime Studies

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To investigate the stability of various atomic arrangements of vacancy aggregates in GaAs, we make use of a self-consistent-charge density-functional-based tight-binding method. In contrast to silicon, where the corresponding number is 6, we find the first such stable aggregate to be made up of 12 vacancies. This is explained by the added possibility of energy lowering Ga-Ga and As-As dimer formation. Since these results are consistent with measured and calculated defect-related positron lifetimes, they give powerful evidence for the existence of such magic number vacancy aggregates in GaAs.

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Although vacancy agglomerates are well known to be produced by “damaging” semiconductors via, e.g., neutron irradiation [1], plastic deformation [2,3], or saw cutting [4], they are also present in, e.g., as-grown silicon [5]. Such vacancies are not only electrically active but also play an important role in the materials’ mechanical properties, such as brittle or ductile fracture [6]. When excess vacancies are mobile but cannot find sinks such as surfaces or dislocations with which to anneal, they are likely to agglomerate—either in a plane, forming a dislocation loop, or into stable three-dimensional (3D) vacancy clusters. While many publications have dealt with this problem in homonuclear materials (C [7], Si [8]), to our knowledge this is the first such study to consider compound semiconductors.

The primary mechanism of vacancy formation during plastic deformation is postulated to be related to dislocation motion (see Fig. 1). Mott [9] has suggested a model of emission or absorption of intrinsic point defects by screw dislocations containing jogs. These jogs can be generated by the intersection of dislocations belonging to different slip systems. Jogs on screw dislocations are not glissile, rather they are forced to follow the glide motion of the screw due to the line tension of the dislocation. During this nonconservative motion of the jog, vacancies or interstitials are emitted (Fig. 1). As a result, one would primarily expect the formation of chains of point defects. However, there is no experimental evidence for the formation of such chains. It has hence been supposed [10] that the clustering of vacancies to stable agglomerates is a primary process of jog dragging. Vacancy chains should thus collapse instantaneously during deformation to form stable clusters. This could happen by atomic rearrangement of vacancies during or immediately after the climb step of the jog.

Positron annihilation spectroscopy (PAS) is a suitable tool to detect small vacancy clusters. Since positron lifetime spectroscopy measures the electron density at the trapping site of the positron, this method is sensitive to the size of open-volume defects, i.e., the positron lifetime increases with increasing open volume [11]. Hence

different types of vacancy-related defects betray “characteristic” positron lifetimes and, therefore, it is possible to distinguish between monovacancies, vacancy chains, and 3D agglomerates. Vacancy agglomerates are generically detected by positron lifetime spectroscopy in deformed semiconductors or metals [2,3,12]. Furthermore, one finds a positron lifetime component which is characteristic for trapping into monovacancies. This defect-related lifetime component has been attributed to vacancy-type defects bound to the dislocation core in Si and Ge [2,3]. In GaAs the corresponding component found is about 260 ps [14]. Widely accepted values for trapping into monovacancies in GaAs (bulk lifetime 230 ps) are dependent on their charge state: 255, . . . 295 ps [13]. The long positron lifetime component of about 500 ps measured in GaAs is an indication of large vacancy agglomerates created during deformation [14].

It is only in covalently bound materials that there exists some indication that stable vacancy clusters of certain sizes should be present. The atomic configurations which have a low number of unsaturated or dangling bonds are considered to be favorable, but which will turn out to be insufficient for compound semiconductors. This led Chadi and Chang [15] to the conclusion that there should be so-called *magic numbers* of vacancies in diamondlike homonuclear structures such as silicon. They proposed stable vacancy clusters for $n = 6, 10,$ and 14 vacancies.

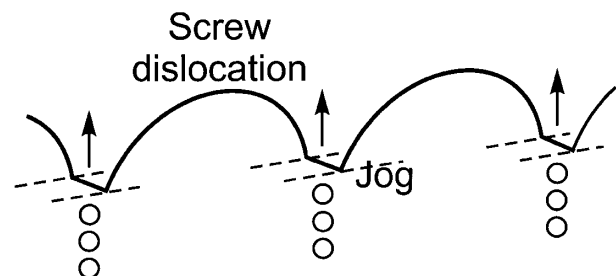


FIG. 1. Formation of point defects (vacancies and interstitials according to the sign of the jog) by the dragging of jogs at screw dislocations.

This may be expanded in a straightforward manner to $n = 4i + 2$; $i = 1, 2, 3, \dots$ since one always has to remove another four atoms in addition to the hexagonal ring to end up with a surface consisting of hexagonal rings (minimum number of dangling bonds). It may now be interesting to investigate whether there exist stable clusters of certain sizes (magic numbers) in compound semiconductors such as GaAs. In contrast to homonuclear systems, the existence of dangling bonds of the different atomic species makes reconstruction and relaxation of the surrounding atoms much more important. Without theoretical calculations, such a conclusion cannot be drawn from experiments such as PAS alone. Therefore, we examine the formation energy for 3D agglomerates as well as for vacancy chains. Furthermore, we calculated the corresponding positron lifetimes to be able to compare our data to experimental results. To avoid defect-defect interactions, we used very large supercells: 512 instead of widely used 64 atoms. Since this cannot be achieved by fully self-consistent field (SCF) methods, one has to apply a more approximative scheme.

A self-consistent-charge density-functional-based tight-binding (SCC-DFTB) method has been used for total energy calculations and structure relaxation. This method employs a basis of numerically derived s and p confined atomic orbitals, which are obtained within the SCF-local density approximation (SCF-LDA). All two-center integrals of the density-functional theory (DFT) Hamiltonian and overlap matrix are evaluated explicitly. Charge transfer is taken into account through the incorporation of self-consistency for the distribution of the Mulliken charges. This is based on a second order expansion of the Kohn-Sham energy. For a detailed description of the SCC-DFTB method and its application to GaAs see Refs. [16–19].

A recent publication, giving very good results for GaAs surface reconstructions [18], as well as test calculations, presented here for the formation energies of mono-vacancies and antisite defects, demonstrates the validity of the SCC-DFTB method in modeling the inner surface of extended vacancy aggregates in GaAs. Indeed, the latter calculations are in very good agreement with SCF-LDA results by Northrup *et al.* [20]; see Table I. This indicates that SCC-DFTB allows calculations of defects with an accuracy comparable to SCF-LDA calculations. We calculate the formation energy of the neutral divacancy to be 5.36 eV.

In contrast to these more sophisticated methods, the computing time and memory usage of SCC-DFTB is up

TABLE I. Defect formation energies ($\Delta\mu = 0$, $\mu_e = 0$) for selected intrinsic point defects.

Method	V_{Ga}^0	V_{Ga}^{3-}	$\text{As}_{\text{Ga}}^{2+}$	Ga_{As}^0	V_{As}^{1+}
LDA [20]	4.55 eV	5.26 eV	0.93 eV	2.74 eV	2.97 eV
SCC-DFTB	4.54 eV	5.58 eV	1.03 eV	2.77 eV	3.09 eV

to 2 orders of magnitude smaller. This allows the modeling of very large supercells, which are needed to avoid defect-defect interaction of such extended defects as considered here. All calculations were done within the Γ -point approximation. We checked the convergence of energy with respect to the number of employed k points. The error in energy was less than 0.02 eV, indicating well-converged results.

In this paper, we limit ourselves to charge-neutral supercells. Although stable vacancy aggregates in GaAs can be charged (which manifests itself in the position of the Fermi level) we do not consider such cases, and we restrict our calculations to vacancy clusters consisting of an equal number of missing arsenic and gallium atoms. The justification comes from the generation mechanism of vacancies by jog dragging. An equal number of V_{Ga} and V_{As} must be produced to recover the dislocation configuration. Because of the electron counting rule, this should lead to configurations which are charge neutral over a wide range of the position of the Fermi level. Additionally, the defect formation energies are then independent of the relative chemical potential and have an absolute value. This allows a direct comparison of the defect formation energies of the vacancy aggregates.

The formation energies Ω_n for neutral defects with an equal number of Ga and As vacancies have been obtained using [21]

$$\Omega_n = E_{\text{tot}} - \mu_{\text{GaAs}}^{\text{bulk}}(n_{\text{Ga}} + n_{\text{As}}), \quad (1)$$

where E_{tot} is the total energy of the supercell containing the defect, n_{Ga} (n_{As}) denotes the number of Ga (As) atoms in the supercell, and $\mu_{\text{GaAs}}^{\text{bulk}}$ is the chemical potential of the Ga and As pair in bulk GaAs, which we obtained in a SCC-DFTB total energy calculation for the GaAs single crystal.

The positron lifetimes for the perfect lattice and for different vacancy cluster configurations are calculated using the superimposed-atom model by Puska and Nieminen in the semiconductor approach (see [11], and references therein). The lattice relaxations under the influence of the trapped positron can be neglected for large open volume defects (cf., e.g., Refs. [22,23]). We took the unrelaxed atomic positions as well as those determined by the SCC-DFTB method. The theoretical data are scaled to the experimental bulk lifetime (a detailed description can be found in [24]).

To be consistent with the deformation experiments in GaAs, the vacancy chains were oriented in a $\langle 121 \rangle$ direction, since this is the direction the jogs are dragged by the gliding screw dislocation in a $\{111\}$ slip plane. In this densely packed direction, zigzag chains of alternating Ga and As vacancies in nearest neighbor positions can be formed.

Our calculations show that the formation energy for chains of vacancies is much higher than that for vacancy clusters (1.4, 3.6, and 5.9 eV for 4, 6, and 8 missing atoms,

i.e., 2, 3, and 4 pairs of V_{Ga} and V_{As}). Hence, if the vacancies are able to move along this vacancy chain, they will rearrange from the initial chain configuration and aggregate as 3D clusters, which have a much lower formation energy. The rearrangement of vacancies should require less energy than a vacancy diffusion in the perfect crystal since less bonds have to be broken for vacancy migration along a vacancy chain. This means that clustering can occur below the temperatures when vacancies become mobile.

We then examined different 3D vacancy aggregates in order to determine the stability of clusters with different numbers of missing atoms. We limited the potentially huge number of possible candidate clusters of up to 14 missing atoms, by noting that only closed structures will have a minimal energy. From the remaining possibilities we made use of a recently published paper [8], which found that, in silicon, hexagonal ringlike structures are energetically most favorable. One possible such configuration is the hexagonal ring consisting of 3 V_{Ga} and 3 V_{As} . The sequence in which the atoms were removed in larger vacancy clusters can be seen in Fig. 3 below. Other configurations which do not follow this straightforward way of construction were checked and found to be significantly higher in energy. They are consequently not considered here.

To compare the energies of the different clusters we calculated the energy gained by adding an isolated divacancy to the most stable aggregate consisting of $n - 2$ vacancies. In our calculations this is

$$\Delta E_n = \Omega_n - (\Omega_{n-2} + \Omega_2),$$

which sets the energy zero at ΔE_2 . Note that ΔE_n is the negative dissociation energy of V_n into $V_{n-2} + V_2$.

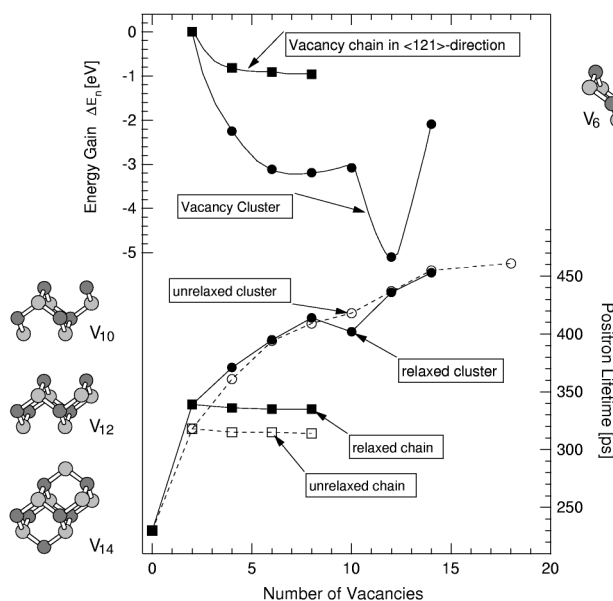


FIG. 2. Energy gained by adding a divacancy to an aggregate of $(n - 2)$ vacancies (upper part) and the corresponding positron lifetime (lower part). Structures of some V_n are shown beside the graphic (As atoms, dark gray; Ga atoms, light gray).

This energy is plotted in Fig. 2 for the most stable aggregates of vacancies. The *smallest* stable structure, with respect to dissociation, is found to be V_{12} in GaAs, whereas in Si it is V_6 (the next proposed stable agglomerates in Si are V_{10} and V_{14}).

We assumed in our calculations that the vacancy aggregates grow by the addition of divacancies. Of course these aggregates can dissociate into other fragments. However, SCC-DFTB predicts the lowest dissociation energies for $V_n \rightarrow V_{n-2} + V_2$.

A general feature of all relaxed structures is that threefold coordinated Ga atoms undergo a sp^2 hybridization by emptying all dangling bonds, whereas all threefold coordinated As atoms show a p^3 bonding configuration with filled dangling bonds. This is typical for GaAs and can be illustrated by the electron counting rule. By following this rule, a Ga atom contributes $3/4$ electrons per bond, whereas As contributes $5/4$ electrons. Since the energy states created by Ga dangling bonds are higher than the energy states by As dangling bonds, the electrons are transferred from gallium to arsenic atoms. As a result the atoms will change the hybridization state to further minimize the total energy.

It can be seen from Fig. 2 that V_{12} is by far the most stable configuration, which can be understood by looking at the relaxed structure of V_{12} in Fig. 3. The dominant feature of this structure is the formation of an As-As and a Ga-Ga dimer ($a-b$, respectively, $c-d$ in Fig. 3). This reduces the number of dangling bonds and, therefore, lowers the total energy. Additionally, it can be seen that the threefold coordinated As atom (a in Fig. 3) is in a p^3 configuration state, whereas the Ga Atom (d in Fig. 3) prefers a planar structure with sp^2 character. Furthermore, Fig. 3 shows that the formation of dimers is already possible for

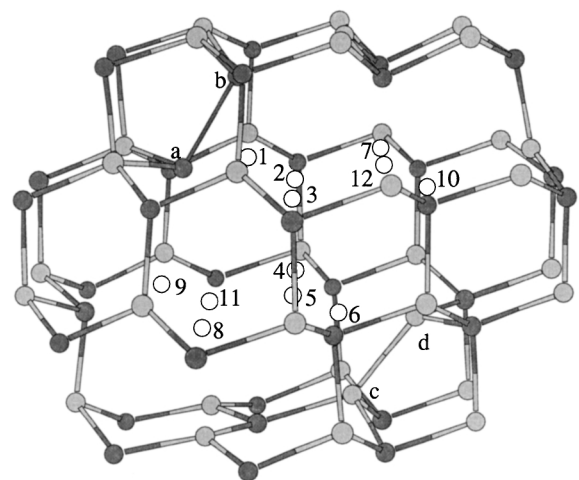


FIG. 3. Structure consisting of 12 vacancies. Dark gray balls denote As and light gray balls denote Ga atoms. The white spheres are the vacancies. The numbers give the order in which the atoms have been removed, starting from V_2 to V_{12} . Atoms a and d are removed to get V_{14} .

V_{10} . However, in contrast to V_{12} , some Ga atoms are not able to form an energetically favorable threefold coordinated sp^2 structure and, therefore, V_{10} is less stable than V_{12} . Further support for the greater stability of V_{12} comes from its significantly larger band gap than the other structures, except the divacancy. In contrast to Si, where one hexagonal ring is the first stable structure, the vacancies in GaAs are arranged here in two hexagonal rings one on top of the other (see Fig. 3).

The dimer formation of inner surface atoms (a - b , respectively, c - d in Fig. 3) is responsible for the lower energy for certain configurations of vacancy agglomerations in compound semiconductors—called *magic number clusters*. Since in GaAs, in contrast to Si, the energy of a structure can already be lowered by transferring electrons from Ga dangling bonds to As dangling bonds, a remarkable reduction of energy can only be achieved when dangling bonds are saturated by dimer formation. This explains why in Si the hexagonal ring with a minimal number of dangling bonds is the first stable cluster, whereas in GaAs it is the double hexagonal (V_{12}) structure, which shows an energetically favorable dimer configuration.

After examining the structure and energetics of the different types of vacancy aggregates we calculated the positron lifetimes for the unrelaxed and relaxed structures. For small clusters (V_2 and V_4) and the vacancy chains the positron lifetime is higher for relaxed clusters compared to unrelaxed ones. This is consistent with an outward relaxation of the atoms surrounding the vacancy cluster (decrease of the electron density). For clusters consisting of more than four vacancies no significant change in positron lifetime before and after relaxation can be observed. An exception is V_{10} , where the unfavorable configuration of some Ga atoms, mentioned above, leads to an increase in the electron density within the open volume. Therefore, we find a reduced positron lifetime after relaxation.

The calculated positron lifetime related to trapping into a zigzag chain of alternating Ga and As vacancies is roughly that of a divacancy, since the electron densities within the open volume are similar.

The increase in the positron lifetime due to the larger open volume of the defects seems to saturate for about 12 to 14 vacancies agglomerated. So, it is difficult to tell from the experimentally observed positron lifetimes if there are even bigger clusters. While the calculations reach their validity limit, the experimental error may be as high as 50 ps for this lifetime component.

In conclusion, the calculations prove that vacancy chains are energetically unfavorable. We can assume that these vacancy chains, generated by jog dragging, collapse instantaneously by atomic rearrangement to 3D vacancy clusters. As a consequence, we find a remarkable new type of *magic number* vacancy clusters in GaAs. We further believe that these results can be generalized also to other III-V semiconductors with zinc blende structure. For the

smallest stable structure we find, in contrast to Si (V_6), for GaAs a V_{12} vacancy cluster consisting of two staggered hexagonal rings. The reason is, unlike the Si case, not only a minimization of the number of dangling bonds, but a lowering of the energy by rehybridization caused by charge transfer from Ga to As. As we find only one stable vacancy cluster configuration up to a size of 12 vacancies, this is a good candidate for the large vacancy agglomerates observed with positron lifetime spectroscopy in deformed GaAs.

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