

Novel diffusion mechanism on the GaAs (001) surface: the role of adatom–dimer interaction

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Employing first principles total energy calculations we have studied the behavior of Ga and Al adatoms on the GaAs(001)- $\beta 2$ surface. The adsorption site and two relevant diffusion channels are identified. The channels are characterized by different adatom–surface dimer interaction. Both affect in a novel way the adatom migration: in one channel the diffusing adatom jumps across the surface dimers and leaves the dimer bonds intact, in the other one the surface dimer bonds are broken. The two channels are taken into account to derive effective adatom diffusion barriers. From the diffusion barriers we conclude a strong diffusion anisotropy for both Al and Ga adatoms with the direction of fastest diffusion parallel to the surface dimers. In agreement with experimental observations we find higher diffusion barriers for Al than for Ga.

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Growth techniques, such as molecular beam epitaxy, operate under conditions far away from thermodynamic equilibrium. Particularly for growth at low temperatures or for structures with length scales smaller than the adatom diffusion length, features driven by the growth kinetics have been observed. [1] In the GaAs/AlAs heteroepitaxy the differences between the growth kinetics of AlAs and GaAs have been utilized to create low dimensional structures. [2] Recently Kapon *et al.* [3] successfully fabricated quantum wire heterostructure in which stimulated emission has been observed.

Despite these successes the underlying microscopic processes such as adsorption, surface diffusion, desorption, and nucleation are poorly understood. A key mechanism in growth is cation surface diffusion which is considered to be a rate limiting process. [4,5] Experimentally the surface diffusion is difficult to access. The deduced migration barriers [6–10] for Ga adatoms span a range between 1.1 and 4.0 eV. Even the anisotropy of surface diffusion on the (001) surface is controversially debated: Shitara *et al.* [11] speculate that fastest diffusion is along the [110] direction; in contrast, Kawabe *et al.* [4] propose the $\bar{1}10$ direction. We have therefore performed first-principles total-energy calculations which constitute a powerful tool to study surface diffusion.

Adatoms on solid surfaces occupy well defined binding sites. The migration of the chemisorbed adatoms can be described as a hopping between these sites. The activation energies for the individual hops are determined

by the energy differences between the binding and the transition sites. These positions can be identified as the minima and saddle points of the potential energy surface over the configurational space spanned by the the coordinates of the adatom and the substrate atoms. In order to find all minima and transition sites a mapping of the entire configurational space is in principle required. However, this is computationally neither possible nor useful. For the study of surface diffusion the mapping is commonly restricted to a subspace given by the lateral coordinates of the adsorbate. [12–16] This mapping gives the potential energy surface (PES) $E(x, y)$ for a given lateral position (x, y) of the adatom where all substrate atoms and the z coordinate of the adatom are fully relaxed. This implies that all minima and saddle points relevant for the description of surface diffusion can be found on one single PES. However, in this Letter the results of our first principles study on the cation diffusivity show that this assumption fails for the migration on the GaAs(001) surface.

In this paper we focus on the GaAs(001)-(2 \times 4) surface in the $\beta 2$ phase. This structure has been shown to be stable at the equilibrium [17] as well as to be the dominating surface structure over a wide range of growth conditions. [18,19] As shown in Fig. 1, each (2 \times 4) unit cell consists of two As dimers and two missing dimers in the topmost layer, a missing Ga pair in the second layer and a As dimer in the third layer.

Our calculations of the PESs employ density functional theory in the generalized gradient approximation (GGA). [20] The electron-ion interaction is described by fully separable, norm-conserving pseudopotentials. [21,22] The adatom-substrate system is modeled by a supercell geometry with a (4 \times 4) periodicity parallel to the surface. This supercell has been tested to be sufficiently large to have a negligible adatom-adatom interaction. Perpendicular to the surface our supercell contains a vacuum of 6 layers GaAs and an additional layer of pseudo H-atoms ($Z=0.75$) to saturate the bonds of the lower surface. [23] To prevent a dipole-dipole interaction between the inequivalent upper and lower surface of our slab we use a dipole correction. [24] The wave functions are expanded in a plane-wave basis with a cutoff energy of 10 Ry. The \mathbf{k} -space integration was performed with a special \mathbf{k} -point set, with a density equivalent to 64 \mathbf{k} -points in the Brillouin zone of the (1 \times 1) surface cell.

The PES has been mapped on an equidistant grid with a spacing of 1 Å along the [110] and the $\bar{1}10$ direction. At each position the upper four substrate layers and the adatom height were fully relaxed, starting from the positions of the clean surface for the substrate and an adatom height of 3 Å above the surface. In a second step we interpolated the PES from the energy values on the mesh. Subsequently we repeated our mapping around the interpolated saddle points using a finer mesh. The exact positions of the local minima were obtained by putting the adatom on the interpolated minima and relaxing *all* atomic positions without constraints.

The resulting PES for a Ga adatom is shown in Fig. 1(a). In each (2×4) unit cell we find the binding sites: \mathbf{A}_1 and the two equivalent positions \mathbf{A}_2 and $\mathbf{A}_{2'}$. All three binding sites are on long bridge positions between surface As-dimer. This agrees with previous first principles calculations [15] for the metastable (2×4) - β structure (assuming near-equilibrium growth conditions [25], at $T = 900$ K, a typical growth temperature, the surface area covered with the $\beta 2$ phase and the area covered by the β phase differ by more than two orders of magnitude). At the three binding sites our calculations yield a strong inward relaxation of the adatom which resides almost in the center between the neighboring As atoms. The substrate atoms display only minor deviations (< 0.2 Å) from their clean surface positions; in particular the surface dimer bonds remain intact.

From PES shown in Fig. 1(a) migration on GaAs(001) can be described as a sequence of random hops on a periodic (2×4) lattice with the three binding sites. The effective diffusion barrier is determined by applying the formalism of continuous time random walk (CTRW) [26] that yields the diffusion tensor as a function of the individual hopping rates between neighboring binding sites. Within transition state theory [27] the individual hopping rate from a site \mathbf{A}_i to a site \mathbf{A}_j via a transition state \mathbf{T}_k can be written as

$$\Gamma_{ij} = \Gamma_{ij}^0 \exp[(E(\mathbf{T}_k) - E(\mathbf{A}_i))/k_B T] \quad (1)$$

where $E(\mathbf{A}_i)$ and $E(\mathbf{T}_k)$ are the energies given in Tab. I. Γ_{ij}^0 is a temperature independent prefactor and assumed to be roughly the same for all individual hops. This assumption leads to only minor errors as long as solely the effective diffusion barrier are discussed. [12,13,15] Applying the CTRW formalism [28] and considering the size of the individual activation energies we find for the diffusion constants along the [110] and $\bar{1}10$ directions

$$D_{[110]} = \frac{\Gamma_{12}\Gamma_{21}(2\Gamma_{22}+\Gamma_{22'})}{(2\Gamma_{12}+\Gamma_{21})(4\Gamma_{22}+\Gamma_{21}+2\Gamma_{22'})} 8a_0^2 \approx \frac{\Gamma_{12}}{2} 8a_0^2 \quad (2)$$

$$D_{\bar{1}10} = \frac{4\Gamma_{12}\Gamma_{22}+\Gamma_{11}\Gamma_{21}}{2\Gamma_{12}+\Gamma_{21}} 2a_0^2 \approx \Gamma_{11} 2a_0^2 \quad (3)$$

a_0 is the lattice constant of GaAs. From the approximated solutions we get as effective diffusion barriers

$\Delta E_{[110]} = E(\mathbf{T}_1) - E(\mathbf{A}_1)$ and $\Delta E_{\bar{1}10} = E(\mathbf{T}_4) - E(\mathbf{A}_1)$, i.e. $\Delta E_{[110]} = 0.8$ eV and $\Delta E_{\bar{1}10} = 0.6$ eV.

In the above discussion we have implicitly assumed that all relevant minima in the configuration space could be found by relaxing the adatom from a position in the vacuum and the substrate from its ideal position in the clean case. This is true if all other minima of the total energy are either energetically much higher or separated from the first minima by a large barrier. The assumption should be correct when the surface exhibits mainly bulk-like bonds, as it is the case for most metal surfaces. For reconstructed semiconductor surfaces, however, surface bonds exist which differ significantly from the bulk bonds, as for example anion-anion dimers. On those surfaces stable adsorption sites for a cation could be realized by breaking these weak surface bonds and forming bulk-like cation-anion bonds instead.

Since in the PES shown in Fig. 1(a) the adatom does not break any surface As-dimer, we investigate in more details the adatom-dimer interaction. Fig. 2(a) shows the binding energy of the adatom as a function of its height z_{a-d} on the dimer center with its lateral coordinates (x, y) fixed above the dimer center [site \mathbf{A}_3 in Fig. 1(b)] and the substrate fully relaxed. Approaching the surface from the vacuum we find a first local minimum at $z_{a-d} \approx 2$ Å which corresponds to a saddle point in the PES shown in Fig. 1(a). Coming closer to the surface there is a barrier at $z_{a-d} \approx 1.2$ Å and another much deeper minimum at $z_{a-d} \approx 0.1$ Å. Such a double potential well was already predicted for Si on Si(001) by Roland and Gilmer. [16] The origin of the barrier and the presence of the second minimum can be understood by analyzing the bonding situation of the adatom to the dimer. At the first minimum the adatom interacts with the completely filled dangling bonds of the dimer [Fig. 2(c)], at the second one it breaks the dimer bond and forms directional bonds with the adjacent anions [Fig. 2(b)]. The barrier between the minima is due to the energy cost required to break the As-dimer. The binding energy at the second minimum is higher than that at the previously found binding sites \mathbf{A}_1 , \mathbf{A}_2 and $\mathbf{A}_{2'}$. This shows that the adsorption site which is defined as the site with the highest binding energy cannot be on the PES displayed in Fig. 1(a).

To find the real adsorption site and to include the influence of the dimer breaking on the diffusion properties we map the PES a second time. In contrast to the mapping of the first PES the adatom height z is now relaxed starting from a position 0.5 Å above the surface and the surface As atoms are relaxed from a initial position where the As-As dimer bond length is 3.5 Å, i.e. the directional dimer bonds are broken. Fig. 1(b) displays the resulting PES. Figs. 1(a) and (b) show that the two PESs are similar over a wide area but they differ significantly around the dimers. In addition to the binding sites already present on the first PES we find

three new binding sites in each unit cell: \mathbf{A}_3 and the two equivalent positions \mathbf{A}_4 and $\mathbf{A}_{4'}$. The comparison of the binding energies of the whole set of binding sites yields as adsorption site \mathbf{A}_3 , a short bridge site between the As atoms of one dimer.

At \mathbf{A}_3 , \mathbf{A}_4 and $\mathbf{A}_{4'}$ the adatom breaks the dimer, and charge accumulations between the adatom and the adjacent anions confirm the formation of directional bonds. The angle between the two adatom-As bonds is about 175° , i.e. the adatom is almost incorporated into the As top layer. This is accompanied by a strong horizontal relaxation of the As atoms bonded to the adatom. They relax along the $[\bar{1}10]$ direction, and the As-As distance increases from $\approx 2.5 \text{ \AA}$ (the As-dimer bond length) to 4.4 \AA which is close to the As-As distance in bulk GaAs (4.0 \AA). The relaxation keeps the nearest neighbor bond length of the substrate atoms nearly unchanged and results in bulk like adatom-As bond lengths. Such a relaxation has been observed experimentally for an Al terminated (2×1) reconstructed GaAs (001) surface. [29] The driving mechanism for the flat incorporation of the cation is analogous to that which leads to the well known inward relaxation of the surface Ga atoms on GaAs(110). The two-fold coordinated adatom with only partially occupied dangling bonds rehybridizes to a planar sp or sp^2 bonding configuration. At the same time the three-fold coordinated As atoms bonded to the adatom gain energy from rehybridization to a p^3 bonding configuration.

To find the exact binding energies at the transition sites \mathbf{T}_5 , \mathbf{T}_6 and \mathbf{T}_7 between the short bridge and the long bridge binding sites the PES has been mapped around the interpolated transition sites as a function not only of the lateral adatom coordinates but also of the dimer atoms. Note that we found an energy barrier to break the dimer for every pathway of the adatom toward \mathbf{A}_3 , \mathbf{A}_4 , and $\mathbf{A}_{4'}$.

Including the new binding sites, surface diffusion is described by a random hopping on a periodic (2×4) lattice with six sites in each unit cell: \mathbf{A}_1 , \mathbf{A}_2 , $\mathbf{A}_{2'}$, \mathbf{A}_3 , \mathbf{A}_4 , and $\mathbf{A}_{4'}$. With the CTRW formalism we approximate the diffusion constants (the rather long exact expression will be published elsewhere [28]) as:

$$D_{[110]} \approx \frac{\Gamma_{12}\Gamma_{31} + \Gamma_{13}\Gamma_{32}}{2\Gamma_{13}} 8a_0^2 \quad (4)$$

$$D_{[\bar{1}10]} \approx \frac{\Gamma_{11}\Gamma_{31}}{\Gamma_{13}} 2a_0^2 \quad (5)$$

From these equations we find as effective diffusion barriers $\Delta E_{[110]} = E(\mathbf{T}_1) - E(\mathbf{A}_3)$ and $\Delta E_{[\bar{1}10]} = E(\mathbf{T}_4) - E(\mathbf{A}_3)$. Inserting the energies given in Tab. I we find for the Ga adatom diffusion $\Delta E_{[110]} = 1.5 \text{ eV}$ and $\Delta E_{[\bar{1}10]} = 1.2 \text{ eV}$. From these values a significant diffusion anisotropy with fastest diffusion parallel to the surface dimers can be concluded.

The inclusion of the binding sites of the second PES changes the diffusion barriers dramatically. At first

glance, taking into account only the second PES seems to be sufficient for the calculation of the diffusion barriers. However, from Eq. (5) it is clear that the description of the diffusion parallel to the surface dimers demands hopping rates from both PESs. If the contributions from one PES are neglected [as in the Eqs. (2) and (3)], wrong barriers are obtained. The reason for involving both PESs is that the energy barrier to hop from a site \mathbf{A}_1 to a site \mathbf{A}_3 (which requires the breaking of a dimer) is only slightly higher than the one to migrate from the site \mathbf{A}_1 to a neighboring \mathbf{A}_1 site. Thus, once an adatom occupies a weakly bound \mathbf{A}_1 site it performs a number of hops to neighboring \mathbf{A}_1 sites (like surfing on the first PES) before being trapped again in a strongly bound \mathbf{A}_3 site.

Our calculated diffusion barriers for a Ga adatom are at the lower limit of the experimentally deduced diffusion barriers ($1.1 - 4.0 \text{ eV}$). This seems reasonable because the experimental results were derived rather indirectly from growth experiments and therefore they are affected by adatom-adatom and adatom-step interactions. Further, the adatom mobility depends on the As supply and decreases with increasing As flux. [30] Accounting for such effects should result in an effective diffusion barrier higher than that calculated here for a single adatom.

We have performed similar calculations also for an Al adatom. The PESs are almost identical to those of a Ga adatom, i.e. the positions of the minima and of the saddle points for the two cations differ by less than 0.1 \AA . The main difference is a slightly stronger corrugation for Al adatoms leading to higher diffusion barriers: $\Delta E_{[110]} = 1.6 \text{ eV}$ and $\Delta E_{[\bar{1}10]} = 1.3$. The enhanced corrugation can be understood in terms of the higher cohesive energy of AlAs ($E_{\text{AlAs}}^{\text{coh}} = 3.78 \text{ eV}$) compared to GaAs ($E_{\text{GaAs}}^{\text{coh}} = 3.26 \text{ eV}$) implying that Al-As bonds are stronger than Ga-As bonds. From the higher barriers we conclude a lower mobility of Al adatoms which is in accordance with several experiments. [1,8] Our calculated difference in the barrier height of about 0.1 eV for Al compared to Ga adatoms agrees rather well with the value of 0.16 eV obtained by Shitara *et al.* [8] from Monte-Carlo simulations of RHEED measurements of the growth of AlAs and GaAs.

In conclusion, we have shown that the adatom-surface dimer interaction is crucial for determining the adsorption site as well as the effective diffusion barrier. The origin of the very stable new adsorption site is that a weak surface bond (As-As) is replaced by almost bulk-like cation-As bonds. This mechanism should also work on other semiconductor surfaces exhibiting surface dimers or trimers.

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TABLE I. Binding energies (eV) of a Ga adatom at various surface sites on the GaAs(001)-(2×4) β2 structure

site	A ₁	A ₂	A ₃	A ₄	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇
Ga	-2.5	-2.2	-3.2	-2.6	-1.7	-1.8	-1.6	-2.0	-1.45	-1.5	-1.9

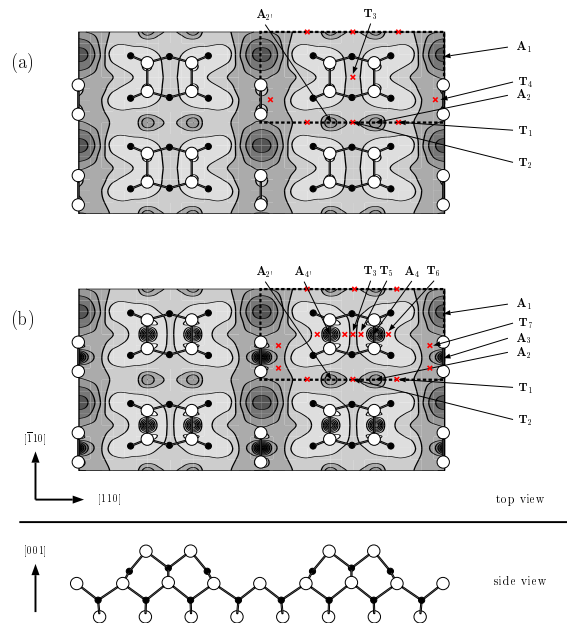


FIG. 1. Total energy surfaces for a Ga adatom on the GaAs(001)-(2×4) β2 surface. (a) PES obtained when the adatom is relaxed from 3 Å above the surface (b) PES obtained when the adatom is relaxed from 0.5 Å above the surface with the surface dimers initially broken. The dashed box shows the unit cell. The contour-line spacing is 0.2 eV. The atomic positions of the clean surface are indicated for atoms of the upper two layers and for the As-dimers in the third layer (As: empty circles, Ga: filled circles).

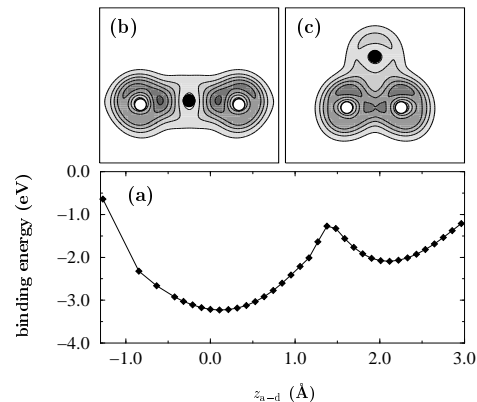


FIG. 2. (a) Binding energy of an Ga adatom as function of its height z_{a-d} above the center of an As-dimer. (b) and (c) charge density cross section through the adatom and the dimer atoms at the two minima of the binding energy.