PHYSICAL REVIEW B **72**, 075315 (2005)

Molecular-dynamics-based model for the formation of arsenic interstitials during low–temperature growth of GaAs

Sándor Kunsági-Máté,[1] Carsten Schür,[2] Eszter Végh,[1] Tamas Marek,[2] and Horst P. Strunk[2]
[1]*Department of General and Physical Chemistry, University of Pécs, Ifjuság útja 6, H-7601 Pécs, Hungary*
[2]*Institute of Microcharacterization, Friedrich-Alexander-University Erlangen-Nuremberg, Cauerstrasse 6, D-91058 Erlangen, Germany*

(Received 14 April 2005; published 4 August 2005)

The formation of interstitial arsenic defects in low-temperature grown (LT) GaAs layers is examined by temperature dependent, direct trajectory molecular dynamics calculations at semiempirical level. In agreement with earlier *ab initio* calculations, a metastable interstitial position of an As_2 molecule just below the As-rich $c(4\times4)\beta$ reconstructed GaAs(001) surface (characterized by As–As dimers) is obtained. We model this conformation as a precursor state for excess interstitial As in the LT-GaAs layers. Furthermore, a migration layer was found above the surface, where As_2 molecules can move practically freely. We identify the hopping of As_2 molecules from the interstitial position into this migration layer as the process that controls the experimentally observed dependencies of the excess arsenic content on substrate temperature and arsenic overpressure during growth of LT-GaAs layers.

DOI: 10.1103/PhysRevB.72.075315 PACS number(s): 68.47.Fg, 61.82.Fk

I. INTRODUCTION

GaAs layers grown by molecular beam epitaxy (MBE) under As overpressure at a substrate temperature below 400 °C (low-temperature grown GaAs, LT-GaAs) are crystalline, but nonstoichiometric due to an appreciable content of excess As, As_{ex}.[1] It is this excess arsenic that gives rise to the very interesting electrical and optical properties of LT-GaAs layers, such as extremely high resistivity and short carrier lifetime.[2,3] The As_{ex} content of LT-GaAs shows an inverse dependence on the growth temperature,[4,5] and increases with the As/Ga flux ratio applied during growth. Under very high As/Ga flux ratio the excess arsenic content saturates at 1.5% for a substrate temperature of about 200 °C on exactly oriented GaAs(001) substrate. This As_{ex} concentration in the LT-GaAs layers is much higher than that derived from the equilibrium phase diagram (0.1% at most), therefore it cannot simply be considered as thermodynamic effect.

The atomistic processes leading to the As_{ex} formation in the growing layer are not completely understood yet. The observed inverse relation between growth temperature and As_{ex} content in LT-GaAs layers indicates that there must be a surface atomic process which reduces the chance of As_{ex} formation with increasing growth temperature. Two plausible candidates discussed already for such a process are the *direct desorption* of As atoms from the adsorption layer into the vacuum[6] and the *escape* of As_2 molecules from specific interstitial positions in the actual growth surface into the adsorption layer.[7,8] The former process has an activation energy of 1 eV,[9] which is too high for the process to occur at appreciable rates at the growth temperature of around 200 °C. The latter process has a low activation energy (64 meV, Ref. 8), which is much more consistent with the experimental value that results from an Arrhenius evaluation to be in the range of 1 meV.[6,8] Therefore two open problems are obvious. First, a contrast between the experimental and theoretical activation energies exists, which could arise from the difference between the *static* theoretical models (i.e., calculation of energy terms at zero temperature) and the experimental situation, which is highly affected by the *dynamics* of the surface processes. Second, the experimentally evaluated activation energy of ~1 meV is extremely low and cannot be due to a simple thermodynamic process, since the kinetic energy of particles is at least fifty times higher in the given growth temperature range. Because of this complexity, we conduct temperature-dependent, direct trajectory molecular dynamics calculations to simulate the kinetic and the thermodynamic processes at the same time. Our approach identifies an atomic process, which is responsible for the excess arsenic formation in LT-GaAs layers.

II. MODELING APPROACH

Ohtake *et al.*[10] have shown that the surface structure of (001) GaAs changes to a $c(4\times4)$ below 480 °C and under high As/Ga flux conditions. It remains unchanged down to room-temperature, showing a 1.75 monolayers (ML) As surface coverage. Ohtake *et al.*, in their recent paper,[11] presented further results on the $c(4\times4)$ structure, which led them to discriminate $c(4\times4)\alpha$ and $c(4\times4)\beta$ surface structures. The $c(4\times4)\alpha$ structure, which is characterized by As–Ga heterodimers, was found during MBE growth under As_4 flux below 500 °C and—partly in coexistence with the $c(4\times4)\beta$ structure—under As_2 flux between 350 and 500 °C growth temperature. Under As_2 flux and below 350 °C growth temperature, the temperature range of LT-GaAs, mainly the $c(4\times4)\beta$ structure, consisting of triplets of As–As dimers, was observed.[11] In fact, our current calculations show that it is only this structure which supports the interstitial As formation.[12]

We represent this $c(4\times4)\beta$ surface reconstruction by a 9 atomic layers thick slab (including reconstruction layer, Fig. 1). For construction of this slab, periodic boundary condi-

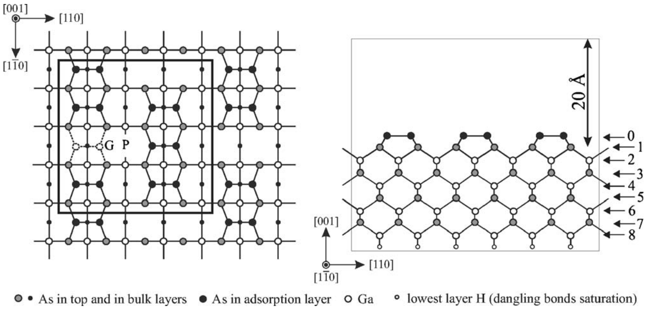

FIG. 1. Top and side view of the cluster for representation of the As-rich $c(4\times4)\beta$ reconstructed GaAs(001) surface. "P" denotes the site where the metastable interstitial position of an As_2 molecule is formed.

tions around a small central box are applied. The central box consists of a volume with size 4×4 in units of $a/2\times\langle110\rangle$ and 2 units of $a\times[001]$ bulk GaAs lattice, with a lattice constant a. The box' surface is covered by the $c(4\times4)\beta$ surface reconstruction layer and contains two reconstruction units. The periodic boundary is applied to the $[-1,1,0]$ and $[1,1,0]$ directions. The atoms of the lowest atomic layer (number 8 in Fig. 1) remain in the positions derived from bulk calculations as a function of temperature (to be published elsewhere) and all atoms within layers above this layer are allowed to move. The atoms at the bottom of this slab are saturated with hydrogen atoms in order to maintain the bulk-like configuration.[8,13]

For explicit simulation of the effect due to the presence of a vapor of As_2 molecules just above the surface, a 20 Å wide region is chosen above the central box, and this region is replicated in the same way as described above by the periodic boundary conditions. The density of the As_2 molecule vapor is adjusted by introducing 5, 10, 15, 20, or 25 As_2 molecules into that volume. These densities are indicated in this work with the symbols P5, P10, P15, P20, and P25, respectively.

The basic reaction studied here is the escape of an As_2 molecule from an energetically metastable interstitial position that has been predicted by earlier works.[7,8] Figures 1 and 2 show the geometry and the escape reaction. During molecular dynamics calculations the height of the lower As atom of the As_2 molecule above the GaAs surface is recorded as a function of the simulation time. The occurrence of an escape reaction is defined at the point when the lower atom of this As_2 molecule crosses the plane of the top arsenic layer of this surface (Fig. 2, denoted by P).

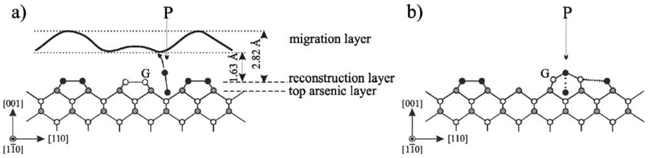

FIG. 2. (a) Schematic view of the geometrical shape of the surface of minimum interaction energy (migration layer) and the escape reaction of an As_2 molecule from the interstitial position in the As-rich $c(4\times4)\beta$ reconstructed GaAs(001) surface. The migration layer refers to the height the center of mass of an As_2 molecule assumes above the plane of the reconstruction layer of the GaAs surface. The upwards pointing, bent arrow symbolizes the escape of an interstitial As_2 molecule into the migration layer; (b) As-interstitial formation on the As-rich $c(4\times4)\beta$ reconstructed GaAs(001) surface due to the formation of a cage by two Ga atoms burying the lower As atom of the As_2 molecule. For definition of the symbols see Fig. 1.

III. CALCULATION PROCEDURE

The interaction energy between the $c(4\times4)\beta$ reconstructed surface and the As_2 molecules is minimized first by variation of the height of the molecule above the surface. During this calculation, the center of mass of an As_2 molecule is fixed to axes oriented perpendicular to the surface, while the free rotation of the molecule around its center is allowed. The intersects of these axes with the surface forms a 20×20 mesh (400 points) above one surface unit cell. Then, the dynamic process between As_2 molecules and the cluster-represented GaAs (001) surface in dependence of the temperature is investigated with Langevin molecular dynamic calculations.[14,15] The PM3 semiempirical quantum chemical method[16–18] is used to calculate atomic forces since parametrization of this PM3 method has been successfully tested in studies of arsenic containing materials[19] and in particular of GaAs crystals.[20,21] The molecular dynamics calculations are done at five different temperatures between 400 and 800 K in steps of 100 K, according to the common temperatures applied in the MBE growth of nonstoichiometric and stoichiometric GaAs layers. Ensembles of $N_0=40$ trajectories with a time resolution of 10 fs are calculated at each given temperature, for a period of 100 ps or until a reaction occurs during propagation of the trajectory.

Reaction rates, k, are determined by fitting k to the calculated fraction of nonreactive trajectories, N/N_0, given by

$$\frac{N}{N_0}=e^{kt}, \tag{1}$$

where t is the reaction time.[22,23] Accordingly, N_0 is the total number of trajectories and N is the number of trajectories without reaction until the time t. Trajectories which do not end with a reaction within the maximum allowed time (100 ps) are counted within N_0. All calculations are carried out with the HyperChem Professional 7 program package[24] and its respective extension[25] for randomization of the As_2 molecules in the volume above the surface.

IV. RESULTS AND DISCUSSION

A. Energetics and geometry

The interaction energies between the As_2 molecules and the $c(4\times4)\beta$ reconstructed As-rich GaAs(001) surface are calculated as described above. All energy versus height curves exhibit a minimum energy value just above the surface. These minimum values represent a surface of minimum energy above the substrate surface which is introduced in Fig. 2. The distance of this minimum energy surface from the reconstruction layer varies between 1.63 and 2.82 Å (Fig. 2).

This surface itself exhibits energy minima that are located just above the middle of the surface trenches running along the [1,–1,0] direction between the triplets of As dimers, thus mimicking the shape of the reconstructed layer (see Fig. 2). The energy barriers between these minima are less than 14 meV. Since the average total kinetic energy of a particle is larger, 52 meV at 400 K and 104 meV at 800 K, As_2 molecules can migrate practically freely on this minimum energy surface, which thus constitutes a migration layer. In correspondence, calculations of trajectories trace such a migration layer. This free movement of As_2 molecules inside the migration layer opposes the formation of any new permanent surface structure, therefore this As-rich $c(4\times4)\beta$ structure remains unchanged. This conclusion is in agreement with experiments according to which not more than 1.75 ML of arsenic coverage exists.[26]

In order to evaluate our present results on the reconstructed $c(4\times4)\beta$ surface with respect to the growth temperature dependence of the excess As content, we apply the model of a Langmuir adsorption-like process. We consider the thermally activated escape of an interstitial As_2 molecule, which acts as precursor to an interstitial As defect, into the migration layer, similar to the method used on the nonreconstructed surface, described in more detail in our earlier work.[8] Our present results show that there is only one position per surface unit cell, closest to one of the As atoms of the middle dimer of the arsenic triplets, which is available as metastable position for a bound As_2 molecule (position P in Figs. 1 and 2). The corresponding fourfold reduction of the surface area for As_2 bonding, as compared to the nonreconstructed surface, results in a four times higher activation energy for the escape process when evaluating experimental data on the growth temperature dependence of the excess As content. Our molecular dynamics calculations indicate that an energy barrier of 54 meV exists for hopping of the bound As_2 molecule from its site into the migration layer (see Fig. 1 and 2) which has to be compared to an experimental activation energy of 4 meV (i.e., four times higher than the previous value of 1 meV, Ref. 6). Additionally, the reverse reaction, where the As_2 molecule jumps back from the migration layer to the interstitial position, has a 17 meV energy barrier, which, however, is negligible considering the growth temperature.

B. Kinetic characteristics

The calculated rate constants, k, of the escape reaction (i.e., hopping from the interstitial site to the migration layer) as derived from the direct trajectory calculations are shown in the Arrhenius plot in Fig. 3. At each of the five given "densities" P, the ln(k) values follow the linear classical Arrhenius equation:

$$\ln(k) = \ln A - \frac{E_a}{k_B T}, \tag{2}$$

where A is the preexponential (frequency) factor, E_a is the activation energy, k_B the Boltzmann constant, and T the temperature. Table I summarizes the Arrhenius parameters obtained by the simulations.

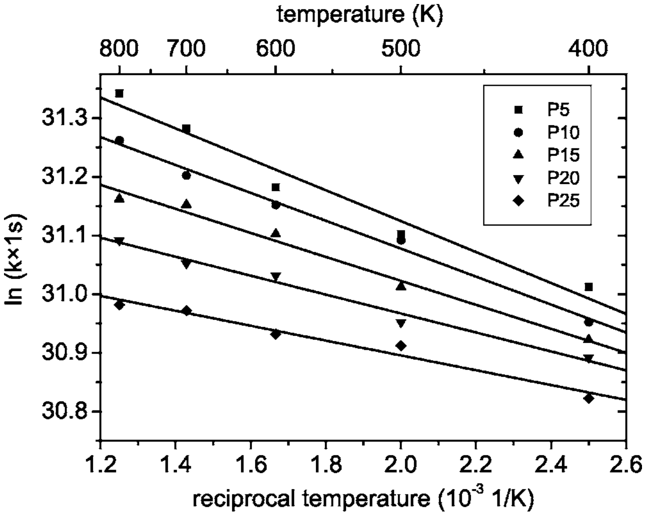

FIG. 3. Arrhenius plot of the rate constants of the reaction associated with the escape of As_2 molecules from the metastable interstitial position observed on the As-rich $c(4\times4)\beta$ reconstructed GaAs(001) surface.

The plots in Fig. 3 reveal that the dependence of the rate constant on the As vapor density above the growing surface is governed by two processes with opposite dependency. First, for any selected growth temperature the rate of the escape reaction decreases with increasing As_2 density. Second, the activation energy [as given by the slopes of the ln(k) lines] for the escape decreases with increasing As_2 density which would mean an increase of the escape rate with increasing As_2 density. For clarification of the responsible processes, more experimental and theoretical investigations are certainly necessary, we may, however, try to understand with the aid of the following notion. We can assume a weak (electrostatic) attractive force between the As_2 molecule in interstitial position and the As_2 molecules in the migration layer, probably supported by the highly negatively charged character of this As covered surface. Furthermore, the number of places in the migration layer is limited and their occupation increases with the As_2 vapor density. This scenario leads to two consequences: Higher density is equivalent to more As_2

TABLE I. Arrhenius parameters for the reaction associated to the escape of As_2 molecules from the metastable interstitial position observed on the As-rich $c(4\times4)\beta$ reconstructed GaAs(001) surface. Symbols P5, P10, P15, P20, and P25 indicate the density of the As_2 molecule vapor above the surface; * value from static calculation, for comparison (Ref. 8).

Symbol of density	Activation energy of escape E_a (meV)	Frequency factor A (1/ps)
P0	64*	—
P5	22.7	55.7
P10	20.5	50.5
P15	17.6	44.7
P20	13.9	38.8
P25	10.9	33.7

in the migration layer and a larger attractive force that would facilitate the escape of the As_2 molecules from the interstitial position. More As_2 in the migration layer means also less free sites and consequently reduces the escape rate. Obviously the calculations indicate that this reduction in escape rates dominates in the examined temperature interval and leads to an increase of filled interstitial sites with increase of As_2 vapor density.

C. Modeling interstitial As formation

One consequence important for modeling is that the escape reaction is very fast, frequency factor is a few tens of 1/ps, see Table I. In comparison, the growth rate commonly applied in experiments is 1 ML/s. Thus we can assume that at any instant of growth the interstitial site population in the growing surface represents the equilibrium population as given by the transition rates into and out of these sites. Growth means that now, under conditions of an As rich atmosphere, also Ga atoms impinge onto the migration layer and onto the growth surface. Our earlier *ab initio* calculations[13] indicated that the middle As dimer of the As_2 dimer triplets is the most reactive center where a newly arriving Ga atom can be incorporated by an exchange reaction with the As there.[13] The present calculations show that the metastable interstitial As_2 site is directly adjacent to this dimer, as in Figs. 1 and 2(a), at P. In a subsequent step, a second Ga atom may fill the adjacent missing dimer site G, see Fig. 1. A cage[7] forms in which the upper As atom of the interstitial As_2 assumes a regular lattice site, see Fig. 2(b). As a result, the lower As atom is buried under a new atomic crystal layer and forms an arsenic interstitial defect in the lattice.

V. SUMMARY AND OUTLOOK

Our simulations of the As-rich growth on the reconstructed $c(4\times4)\beta$ GaAs(001) surface at rather low temperature indicate enhanced surface diffusion of the As_2 molecules in a migration layer situated approximately one atomic distance above the reconstruction layer. From this migration layer, As_2 molecules will enter into the crystal onto a metastable position of specific type. In this position the lower As atom of an As_2 molecule fills a tetrahedral interstitial site. The rate constant of the escape of an As_2 molecule from this position into the migration layer is smaller at lower temperature and higher arsenic vapor density. Accordingly, the lifetime of such an interstitial conformation increases when the growth temperature is lowered or the arsenic As_2 vapor density, i.e., arsenic overpressure during growth is increased. From this conformation interstitial excess arsenic can easily be formed by a cage-like conformation, induced by arriving Ga atoms.[7,8] A next step could transform the As-interstitials to As-antisites, which prevail in LT-GaAs. So we propose this sequence as a very probable way for excess As formation during the low-temperature MBE growth of GaAs layers.

It is interesting in view of our presented calculations to consider the recent result of Ohtake *et al.*[11] that the surface reconstruction changes above 350 °C to a structure essentially characterized by As–Ga heterodimers. Our ongoing respective calculations show that the presented interstitial As formation process is hindered by As–Ga heterodimers because the approaching As_2 molecule cannot reach the interstitial position at the Ga-side of the heterodimer.[12] As a matter of fact, the excess As content is observed to reduce to the value of standard GaAs above this temperature.[27]

ACKNOWLEDGMENTS

This work was financially supported by MÖB (Magyar Ösztöndíj Bizottság) and DAAD (Deutscher Akademischer Austauschdienst). A part of the calculations was performed on SunFire 15000 Supercomputer in the Supercomputer Center of the Hungarian National Infrastructure Development Program Office.

---

[1] *Low Temperature GaAs and Related Materials*, edited by G. L. Witt *et al.*, MRS Symposia Proceedings (Material Research Society, Pittsburg, 1992), Vol. 241.

[2] *Symposium on Non-Stoichiometric III-V Compounds*, edited by P. Kiesel *et al.*, Series Physik Mikrostrukturierter Halbleiter (Friedrich-Alexander-Universität, Erlangen, 1998), Vol. 6.

[3] *Second Symposium on Non-Stoichiometric III-V Compounds*, edited by T. Marek *et al.*, Series Physik Mikrostrukturierter Halbleiter (Friedrich-Alexander-Universität, Erlangen, 1999), Vol. 10.

[4] M. Luysberg, H. Sohn, A. Prasad, P. Specht, Z. Liliental-Weber, and E. R. Weber, J. Appl. Phys. **83**, 561 (1998).

[5] A. Suda and N. Otsuka, Appl. Phys. Lett. **73**, 1529 (1998).

[6] A. Suda and N. Otsuka, Surf. Sci. **458**, 162 (2000).

[7] T. Marek, S. Kunsagi-Mate, and H. P. Strunk, J. Appl. Phys. **89**, 6519 (2001).

[8] S. Kunsagi-Mate, T. Marek, C. Schür, and H. P. Strunk, Surf. Sci. **515**, 219 (2002).

[9] K. Shiraishi and T. Ito, Phys. Rev. B **57**, 6301 (1998).

[10] A. Ohtake, J. Nakamura, S. Tsukamoto, N. Koguchi, and A. Natori, Phys. Rev. Lett. **89**, 206102 (2002).

[11] A. Ohtake, P. Kocan, J. Nakamura, A. Natori, and N. Koguchi, Phys. Rev. Lett. **92**, 236105 (2004).

[12] S. Kunsági-Máté, C. Schür, T. Marek, and H. P. Strunk (unpublished).

[13] S. Kunsági-Máté, C. Schür, T. Marek, and H. P. Strunk, Phys. Rev. B **69**, 193301 (2004).

[14] W. F. van Gunsteren and H. J. C. Berendsen, Angew. Chem. **29**, 992 (1990).

[15] M. Karplus and G. A. Petsko, Nature (London) **347**, 631 (1990).

[16] J. J. P. Stewart, J. Comput.-Aided Mol. Des. **4**, 1 (1990).

[17] J. J. P. Stewart, J. Comput. Chem. **10**, 209 (1989).

[18] J. J. P. Stewart, J. Comput. Chem. **10**, 221 (1989).

[19] A. N. Pankratov and I. M. Uchaeva, J. Mol. Struct.: THEOCHEM **498**, 247 (2000).

[20] Ş. Erkoç and L. Türker, Physica E (Amsterdam) **5**, 7 (1999).

[21] A. M. Mazzone, Nucl. Instrum. Methods Phys. Res. B **142**, 17 (1998).

[22] K. R. Wright and X. Zhao, Chem. Phys. Lett. **246**, 387 (1995).

[23] S. Kunsági-Máté, E. Végh, G. Nagy, and L. Kollár, Chem. Phys. Lett. **388**, 84 (2004).

[24] *HyperChem Professional 7*, Hypercube Inc., 2002.

[25] T. Bender, "Solvent Cage," *Excel Macros to HyperChem*, Hypercube, 2000, www.hyper.com.

[26] J. R. Creighton and K.C. Baucom, Surf. Sci. **409**, 372 (1998).

[27] M. R. Melloch, N. Otsuka, K. Mahalingam, A. C. Warren, J. M. Woddall, and P. D. Kirchner, Mater. Res. Soc. Symp. Proc. **241**, 113 (1992).