A first-principles surface phase diagram study for Si-adsorption processes on GaAs(111)A surfaces

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Abstract

The adsorption processes of an Si atom on GaAs(111)A surfaces under growth conditions are investigated on the basis of first-principles surface phase diagrams, in which adsorption-desorption behavior is described by comparing the calculated adsorption energy obtained by total-energy electronic-structure calculations with vapor-phase chemical potential estimated by quantum statistical mechanics. The calculated surface phase diagram as functions of temperature and As_2 pressure demonstrates that both Ga and As atoms are adsorbed on the Ga-vacancy site of GaAs(111)A-(2×2) surface under low As-pressure conditions, resulting in the formation of (2×2) surface with an As adatom. The surface phase diagrams as functions of temperature and Si pressure also reveal that an Si atom can be adsorbed on the (2×2) surface with an As adatom for temperatures less than ∼1160 K and this Si atom can occupy one of As-lattice sites after the incorporation of another As atom, leading to p-type conductivity. In contrast, the (2×2) surface with an As trimer is found to be stabilized under high As-pressure conditions. The surface phase diagram for Si incorporation clarify that an Si atom can be adsorbed at one of Ga-lattice sites of the (2×2) surface with an As trimer for temperatures less than ∼870 K. These calculated results provide one of possible explanations for the formation of p-type and n-type GaAs on GaAs(111)A surfaces under low and high As-pressure conditions, respectively.

Key words: GaAs(111)A surface; Si doping; Surface phase diagrams; Electron counting rule
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1 Introduction

The control of dopant incorporation on Ga-terminated GaAs(111)A surfaces is important for the epitaxial growth of nanostructures such as quantum wires and quantum dots. Regarding the incorporation processes of dopants such as Si, several experimental studies have shown that the molecular-beam epitaxy (MBE) growth on GaAs(111)A surfaces is different from that on (001) surfaces: [1–4] The Si-doped GaAs exhibits p-type conductivity when it is grown under conventional MBE growth condition whereas it becomes n-type under extremely high As overpressure. [5,6] This phenomenon implies that the incorporation processes of Si atoms on GaAs(111)A surfaces depend on the growth condition. To clarify the amphoteric nature of GaAs layers grown on GaAs(111)A surface, it is thus necessary to clarify the Si incorporation processes on GaAs(111)A surfaces considering the growth condition such as beam equivalent pressure (BEP).

Previous theoretical calculations have clarified that the stable adsorption site of a single Si adatom on GaAs(111)A surface is the empty Ga-lattice (V_{Ga}) site of GaAs(111)A-(2×2) with Ga vacancy. [7] Despite these findings, there have been very few theoretical studies on the Si-incorporation processes during thin film growth on GaAs(111)A surfaces taking account of the growth conditions such as BEP and temperature: The microscopic origins why the Si adatom occupies different lattice sites depending on the growth conditions are still unclear.

In this study, the adsorption processes of Si on GaAs(111)A surface under growth conditions are investigated on the basis of first-principles surface phase diagrams. Since the surface reconstructions are one of important factors which determine the growth kinetics of epitaxial growth, we clarify the reconstructions of GaAs(111)A under growth conditions using our first-principles approach in which surface phase diagrams depending on temperature and pres-

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sure are described by comparing the calculated adsorption energy with vapor-phase chemical potential estimated by quantum statistical mechanics. The calculated surface phase diagram as functions of temperature and As_2 pressure demonstrates that both Ga and As atoms are found to be adsorbed on the surface with Ga-vacancy under low As_2-pressure conditions, whereas the surface with an As trimer is stabilized under high As_2-pressure conditions. For low As_2-pressure conditions, the surface phase diagram as functions of temperature and Si pressure reveals that an Si atom can be adsorbed for temperatures less than ∼1160 K and occupies one of As-lattice sites by forming a trimer consisting of one Si and two As atoms (Si-2As trimer, hereafter). For high As_2-pressure conditions, an Si atom can be adsorbed at one of Ga-lattice sites of the (2×2) surface with an As trimer for temperatures less than ∼870 K. These calculated results imply that both surface reconstructions and adsorption processes under growth conditions are of significance to elucidate doping processes on GaAs(111)A surfaces.

In the next section we describe our methodology, and Sec. 3 contains the main results and discussion. The surface reconstructions of GaAs(111)A surfaces under growth conditions are discussed in Sec. 3.1. The Si incorporation processes taking account of the reconstructions under low and high As_2-pressure conditions are described in Sec. 3.2 and Sec. 3.3, respectively.

2 Calculation procedure

In this study, the adsorption-desorption behavior of Si and As atoms is described by comparing the chemical potential of adsorbent μ_{solid} with that of its molecular species in vapor phase μ_{gas}. Here, μ_{solid} is obtained using the adsorption energy, which is calculated by the energy difference between the stable structures with and without adsorbent. This value can be obtained by the total-energy calculations within density functional theory. μ_{gas} is calculated by the following procedure: μ_{gas} of Si atom and As_2 molecule in vapor phase (μ_{gas}^{Si} and $\mu_{gas}^{\mathrm{As_2}}$, respectively) are given by, [8,9]

$$\mu_{gas}^{\mathrm{Si}} = -k_B T \ln\left\{\frac{k_B T}{p_{\mathrm{Si}}} \times g\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right\}, \quad (1)$$

$$\mu_{gas}^{\mathrm{As_2}} = -k_B T \ln\left\{\frac{k_B T}{p_{\mathrm{As_2}}} \times g\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \times \zeta_{rot} \times \zeta_{vib}\right\}, \quad (2)$$

where k_B is the Boltzmann constant, T is the gas temperature, g is the degree of degeneracy of electron energy level, and p_{Si} ($p_{\mathrm{As_2}}$) is the BEP of Si atom ($\mathrm{As_2}$ molecule). ζ_{rot} and ζ_{vib} are the partition functions for rotational and vibrational motions, respectively. Using μ_{gas} and μ_{solid}, the adsorption and desorption behaviors of adsorbents on GaAs(111)A-(2×2) surfaces under growth condition are obtained as functions of temperature and pressure, *i.e.*, the adsorption occurs when μ_{solid} is lower than μ_{gas}, whereas the desorption occurs when μ_{gas} is lower than μ_{solid}. The calculated surface phase diagrams of GaAs(111)A-(2×2) surfaces are then obtained based on these comparisons.

Total-energy calculations are performed within plane-wave pseudopotential approach using the generalized gradient approximation of GGA-PBE exchange correlation functional. [10] We use norm-conserving pseudopotentials to describe the electron-ion interaction [11] and 3d electrons for Ga atoms are treated by using partial core corrections. [12] The conjugate-gradient minimization technique is used for both electronic-structure calculation and geometry optimization. [13] The valence wave functions are expanded by the plane wave basis set with a cutoff energy of 12.25 Ry. The (2×2) slab model with four bilayers of GaAs and a vacuum region equivalent to nine atomic layer thickness is adopted. The bottom surface is terminated by artificial H atoms. [14] The 9-k points are employed to sample the irreducible Brillouin zone for the (2×2) unit cell.

3 Results and discussion

3.1 Reconstructions of GaAs(111)A surfaces

It is well known that GaAs(111)A surface takes the (2×2) reconstruction with Ga vacancy under various conditions. However, it also forms the (2×2) with

As-trimer under As-rich condition. [15] This indicates that reconstructions on GaAs(111)A surfaces depends on the growth conditions such as temperature and As pressure. In order to clarify the reconstructions during the MBE growth conditions, we calculate surface phase diagram of GaAs(111)A surfaces by assuming that the pressure of Ga atom in vapor phase is $\sim 10^{-7}$ Torr. [16] The phase diagram for Ga adsorption on the (2×2) with Ga vacancy clarifies that Ga atoms itself cannot be adsorbed on the surface for temperatures higher than 600 K (not shown here). Instead, when an As atom reside above the hollow site near V_{Ga}, an Ga atom can be adsorbed at the V_{Ga} site. Figure 1 shows the calculated phase diagram of the GaAs(111)A-(2×2) surfaces as functions of temperature and As_2 pressure. The surface with an As adatom is stabilized for temperatures less than 1030 K. [17] The promotion of Ga adsorption caused by As atoms is due to the reduction of Ga-adsorption energy by self-surfactant effect, [18] as shown in Table 1: For the (2×2) surface with an As adatom, excess electrons on Ga-dangling bonds can be eliminated by satisfying the electron counting rule. [19]

Furthermore, the phase diagram shows that the surface with an As trimer is stabilized for As-rich (high As_2 pressure and low temperature) conditions, consistent with the scanning tunneling microscopy observation of As trimer under As-rich conditions. [15] Since the surface with As adatom is favorable for p_{As_2} less than $\sim 10^{-5}$ Torr around 800 K, the Si-doping processes in the MBE with low As pressure should be examined by the adsorption of Si atoms on the (2×2) surface with an As adatom. Due to the appearance of the As-trimer surface for p_{As_2} larger than $\sim 10^{-5}$ Torr, on the other hand, the processes with high As pressure should be discussed on the basis of Si adsorption on the (2×2) surface with As trimer. In the subsequent subsections, we define low As-pressure conditions as $p_{As_2} \leq 1\times 10^{-5}$ Torr and high As-pressure conditions as $p_{As_2} \geq 1\times 10^{-5}$ Torr .

3.2 Si adsorption under low As-pressure conditions

On the basis of surface reconstructions under growth conditions obtained in Sec. 3.1, we examine the adsorption behavior of Si on GaAs(111)A surfaces

under low p_{As_2} conditions using the (2×2) surface with an As adatom. Here, we consider the adsorption of a single Si atom on the (2×2) surface because the flux intensity of Si during doping is likely to be much smaller than those of Ga and As. Our calculations for the stable structures of Si-incorporated surfaces demonstrate that the most stable adsorption site of a single Si atom is found to be located at between topmost Ga atoms near the As adatom, forming an Si-As dimer. Table 1 shows calculated adsorption energies of adsorbent atoms on the (2×2) surface with an As adatom. The adsorption energy of Si atom (−4.45 eV) is found to be lower than those of Ga and As atoms (−2.26 and −1.68 eV, respectively). Therefore, Si atoms are preferentially adsorbed on the surface, resulting in the formation of precursive Si-As dimer structure toward *p*-type GaAs formation. [20] The surface with an Si-As dimer is stabilized satisfying the electron counting rule, [19] while there is one excess and deficit electron on Ga and As dangling bonds for the surface with Ga-As and As-As dimers, respectively. Indeed, the calculated band structure of the surface with an Si-As dimer exhibits semiconducting character.

Figure 2 shows the calculated phase diagram for Si adsorption on the (2×2) surface with an As adatom as functions of temperature and Si pressure. The surface with an Si-As dimer shown in schematic topview of Fig. 2 is stabilized for temperatures less than ∼1160 K. This temperature range clearly manifests that under temperature range of MBE with low As-pressure (red area in Fig. 2) the Si atom is incorporated on the surface and forms Si-As dimer. However, the Si adatom does not occupy As-lattice sites. Only by means of this precursive structure, the formation of GaAs with *p*-type conductivity cannot be explained.

Further adsorption processes on the precursive surface with an Si-As dimer enable the formation of Si adatom occupying one of As-lattice sites occurs under growth condition. Figure 3 shows the calculated phase diagram of As adsorption on the (2×2) surface with an Si-As dimer as functions of temperature and As_2 pressure. As a results of the As adsorption, the surface forms a trimer consisting of one Si and two As atoms (schematic topview of Fig. 3). The Si atom is located above one of topmost Ga atoms occupying one of As-lattice sites. The adsorption energy of As atom (−2.73 eV shown in

Table 1) corresponds to phase boundary between the surface with an Si-As dimer and that with an Si-2As trimer around 1150 K. The surface with an Si-2As trimer is stabilized for temperatures less than ∼1150 K, implying that under temperature range of the MBE with low As-pressure (red area in Fig. 3) As atoms are adsorbed and Si-As trimers in which Si adatoms occupy As-lattice sites can be formed after the incorporation of Si atoms. These series of Si-adsorption processes are reasonably consistent with the experimental fact that GaAs layers under conventional MBE growth conditions exhibit p-type conductivity.

3.3 Si adsorption under high As-pressure conditions

We here examine the adsorption behavior of a single Si atoms on GaAs(111)A surfaces under high $p_{\mathrm{As_2}}$ conditions using the (2×2) surface with an As trimer. Our calculations for the stable structures of Si-incorporated surfaces demonstrate that the most stable adsorption site of a single Si atom is located above the As trimer. Since the Si adatom occupy one of Ga-lattice sites, this adsorption process results in the formation of GaAs with n-type conductivity. Table 1 also shows calculated adsorption energies of adsorbent atoms on the (2×2) surface with an As trimer. The adsorption energy of Si atom (−3.23 eV) is lower than those of Ga and As atoms (−2.44 and −1.62 eV, respectively), indicating that Si atoms are preferentially adsorbed on the surface. The Si-adsorbed As trimer is stabilized satisfying the electron counting rule, [19] while there is one excess and deficit electron on Ga and As dangling bonds of Ga and As adatoms, respectively.

Figure 4 shows the calculated phase diagram for Si adsorption on the (2×2) surface with an As trimer as functions of temperature and Si pressure. The Si-adsorbed surface with an As trimer shown in schematic topview of Fig. 4 is stabilized for temperatures less than ∼870 K. This temperature range clearly shows that under temperature range of MBE with high As-pressure (red area in Fig. 2) the Si atom is incorporated on the surface and occupies one of Ga-lattice sites. Therefore, the calculated Si-adsorption process for high $p_{\mathrm{As_2}}$ larger than $\sim 10^{-5}$ Torr is consistent with the experimental results of GaAs

formation with n-type conductivity under extremely high As overpressure.

4 Summary

We have investigated the Si-adsorption processes on GaAs(111)A surfaces under growth conditions using first-principles surface phase diagrams. We have found that the (2×2) surface with As adatoms is stabilized under low As_2-pressure conditions while the surface with an As trimer is favorable under high As_2-pressure conditions. This implies that the Si adsorption for low As-pressure conditions occurs on the surface with an As adatom and that for high As-pressure conditions does on the surface with an As trimer. For low As_2-pressure conditions, the surface phase diagram as functions of temperature and Si pressure has revealed that an Si atom can be adsorbed on the (2×2) surface with an As adatom for temperatures less than 1000-1300 K. The Si adatom can occupy one of As-lattice sites by forming a trimer consisting of one Si and two As atoms. For high As_2-pressure conditions, the Si atom can be adsorbed at one of Ga-lattice sites of the (2×2) surface with an As trimer for temperatures less than ∼870 K. These results thus suggest that the formation of GaAs layers with p-type and n-type conductivity on GaAs(111)A surfaces can be explained in terms of the adsorption of Si adatoms at the As and Ga lattice sites under low and high As-pressure conditions, respectively.

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[16] Same expression as Eq. (1) is applied to estimate the chemical potential of Ga atom in vapor phase.

[17] If we assume low pressure conditions for Ga atom ($\sim 10^{-10}$ Torr), the temperature range stabilizing the As-adatom surface becomes less than 830 K and the surface with Ga vacancy appears beyond 830 K. Although the value

of the temperature is higher than the experimentally reported one (670 K), this is qualitatively consistent with the experimental results in which the (2×2) surface with Ga vacancy appears at lower temperatures under high V/III flux ratio conditions. See, A. Ohtake, J. Nakamura, T. Komura, T. Hanada, T. Yao, H. Kuramochi, M. Ozeki. Phys. Rev. B **64** (2001) 45318.

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[20] The Si atoms do not require any co-adsorption atoms if the surface posseseses As atoms.

Table 1

Calculated adsorption energy E_{ad} (in eV) and excess electrons on dangling bonds before and after the adsorption, $Z_{\rm before}$ and $Z_{\rm after}$, for various adsorbent atoms. The positive and negative sign in $Z_{\rm before}$ and $Z_{\rm after}$ indicate excess and deficit electrons on Ga (Si) dangling and As dangling bonds, respectively ($Z_{\rm before}$=$Z_{\rm after}$=0 satisfies the electron counting rule).

Surface	Adsorbent atom	E_{ad}	$Z_{\rm before}$	$Z_{\rm after}$
(2×2) with Ga vacancy	Ga	−1.69	0	+3
(2×2) with Ga vacancy and As adatom	Ga	−3.56	−3	0
(2×2) with As adatom	Ga	−2.26	0	+1
(2×2) with As adatom	As	−1.68	0	−1
(2×2) with As adatom	Si	−4.50	0	0
(2×2) with Si-As dimer	As	−2.73	0	+1
(2×2) with As trimer	Ga	−2.44	0	+1
(2×2) with As trimer	As	−1.62	0	−1
(2×2) with As trimer	Si	−3.23	0	0

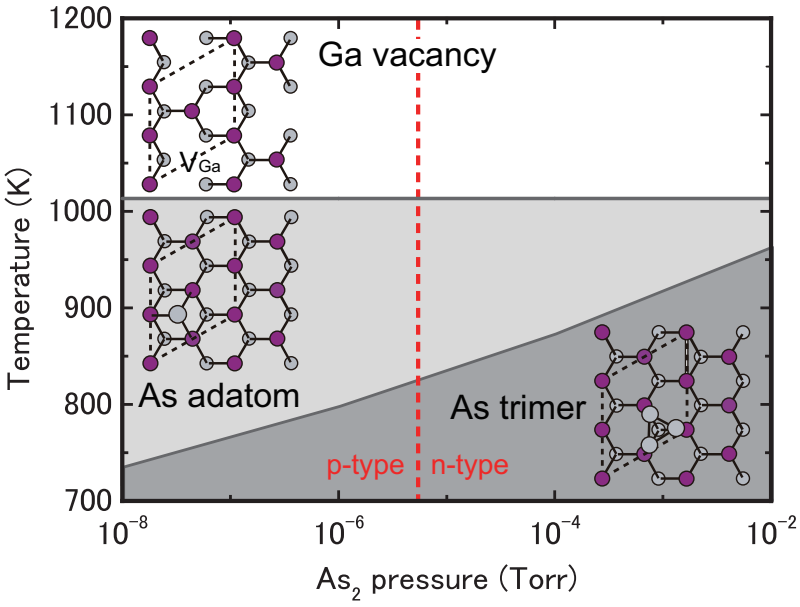

Fig. 1. (Color online) Calculated surface phase diagram among GaAs(111)A-(2×2) surface with Ga-vacancy (Vs_{Ga}), the surface with an As adatom, and the surface with an As-trimer, as functions of temperature and As_2 pressure. The As-pressure boundary between p-type and n-type GaAs growth in the MBE (at 770-870 K) [6] is shown by red (dashed) line. Ga and As atoms are represented by purple (filled) and gray (empty) circles. The unit cell is shown by dashed rhombus.

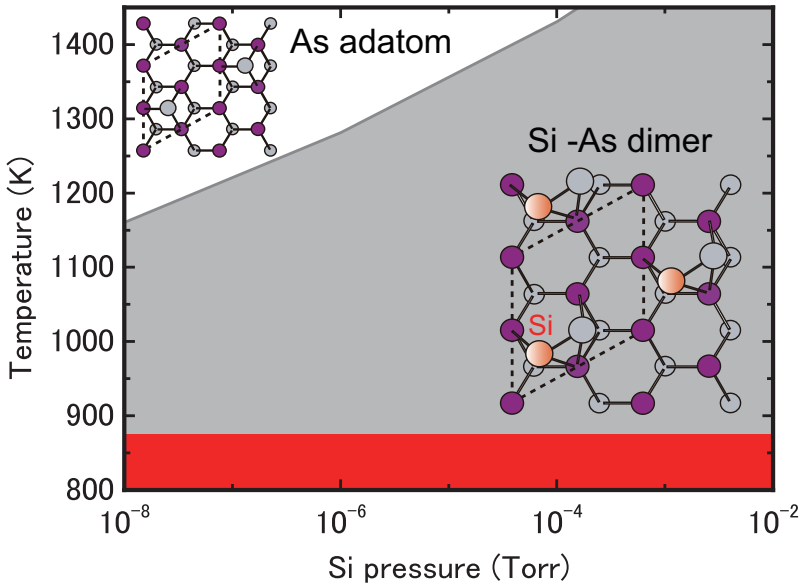

Fig. 2. (Color online) Calculated surface phase diagram between GaAs(111)*A*-(2×2) surface with an As adatom and the surface with an Si-As dimer, as functions of temperature and Si pressure. The experimental temperature range (770-870 K) [6] is shown by red (dark gray) area. Si, Ga and As atoms are represented by orange (gray), purple (filled) and gray (empty) circles. The unit cell is shown by dashed rhombus.

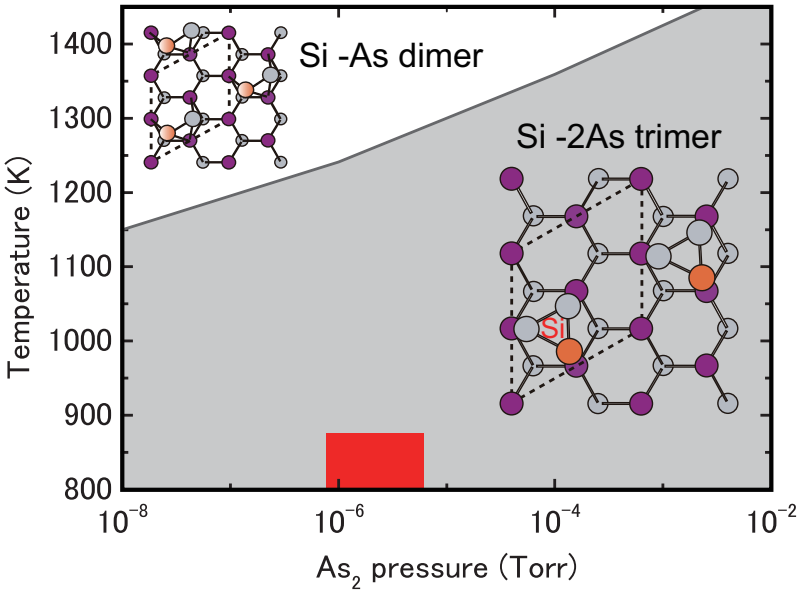

Fig. 3. (Color online) Calculated surface phase diagram between GaAs(111)A-(2×2) surface with an Si-As dimer and the surface with an Si-2As trimer, as functions of temperature and As_2 pressure. The experimental growth conditions for the fabrication fo p-type GaAs (770-870 K at $\sim 5\times10^{-6}$ Torr) [6] is shown by red (dark gray) area. Si, Ga and As atoms are represented by orange (gray), purple (filled) and gray (empty) circles. The unit cell is shown by dashed rhombus.

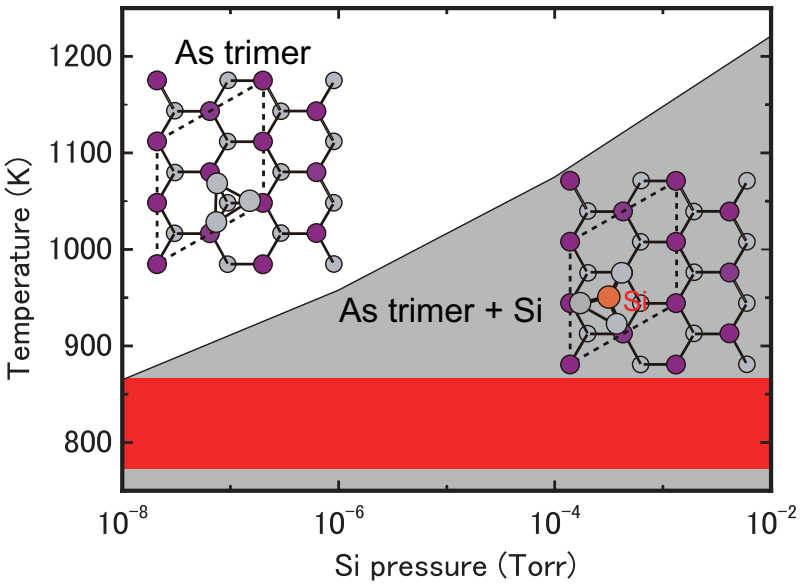

Fig. 4. (Color online) Calculated surface phase diagram between GaAs(111)A-(2×2) surface with an As trimer and Si-incorporated surface with an As trimer (As trimer+Si), as functions of temperature and Si pressure. The experimental temperature range (770-870 K) [6] is shown by red (dark gray) area. Si, Ga and As atoms are represented by orange (gray), purple (filled) and gray (empty) circles. The unit cell is shown by dashed rhombus.