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Ab initio modelling of In wetting layer formation on As-stabilized GaAs during first stages of droplet epitaxy

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Abstract. In this work we carry out theoretical study of the formation of an In wetting layer on the surface of As-stabilized GaAs(001)-(1×1) to better understand the growth kinetics of metal droplets during droplet epitaxy. For this study, we calculate the dependence of the adatom adsorption energy (Eads) on the In coverage, since its value describes force with which adatoms interact with substrates, directly affecting their mobility. Calculations were performed using the state-of-the-art approaches of the density functional theory. The results show that at 0.125 ML coverage Eads has very high value of 8.48 eV which is explained by the adsorbate induced surface reconstruction being included in calculated value. With increasing coverage Eads dropped significantly (down to 3.588 eV/adatom at 1.75 ML coverage) which can lead to subsequent adatoms having greater mobility and can affect the size and surface density of metal nanodroplets and quantum dots based on them.

Keywords: density functional theory, GaAs, indium, adsorption energy, critical thickness, droplet epitaxy, molecular beam epitaxy

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Материалы конференции

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Моделирование начальных этапов формирования смачивающего слоя индия на As-стабилизированной подложке GaAs из первых принципов

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Аннотация. В данной работе представлены результаты теоретического исследования процесса формирования смачивающего слоя индия на As-стабилизированной поверхности GaAs(001) во время капельной эпитаксии. Результаты показывают, что с увеличением степени покрытия поверхности сила связи адатомов смачивающего слоя с подложкой значительно падает, что приводит к увеличению их подвижности, влияющей на размер и распределение металлических нанокapель и получаемых из них квантовых точек.

Ключевые слова: теория функционала плотности, GaAs, индий, энергия адсорбции, критическая толщина, молекулярно-лучевая эпитаксия

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Introduction

Epitaxial growth of nanostructures on surface of III-V compounds is currently one of the most promising directions in nanoelectronics and nanophotonics. At the same time, the question of how to control the kinetics of growth processes still remains relevant due to the diversity of the studied systems and growth mechanisms. Droplet epitaxy [1] is flexible method for growth of quantum dots (QD) allowing to independently control shape, size, and density of resulting self-assembled nanostructures. It relies on formation of metal nanodroplets from thin wetting layer of group III elements which then are crystallized by annealing in group-V element flux. The initial stage of the wetting layer formation, which strongly depends on the specifics of interactions between adatoms and continuously changing substrate, is crucial in this process as it defines the size and distribution of the resulting crystalline QDs. The geometric parameters of the droplets formed are determined by the critical thickness of the wetting layer and the adatom mobility both of which strongly depend on the temperature [2, 3] and the nature of bonds formed between the substrate and the wetting layer. The strength of these bonds can generally be described by the adsorption energy.

In this work, we calculate the adsorption energy of the In wetting layer forming on the As-stabilized GaAs surface at different substrate coverages in order to describe the change in the strength of the bonds that it forms with surface in the early stages of its growth.

Methods

Ab initio calculations of F-43m GaAs(001)-(1×1) slab model (Fig. 1) were performed using density functional theory (DFT). It was applied by using the Vienna ab initio simulation package (VASP) [4] with the projector augmented wave potential construction. For approximating the exchange-correlation functional we used Perdew-Burke-Ernzerhof model based on generalized-gradient-approximation (PBE) [5]. DFT+U method based on Dudarev's approach [6] was used to properly describe interactions of d-band electrons. DFT-D2 method of Grimme [7] was used to correct van der Waals interactions. The dipole correction [8] was found to have a negligible effect on these calculations and was not used in this work.

Simulation cell volume of clean GaAs was optimized for set calculation parameters with resulting lattice constant of 5.497 Å. The atom positions in 2×2×4 simulation cell were optimized using a conjugate gradient algorithm with lower 8 layers (out of 18) fixed until the forces were below 0.02 eV/Å. Each adsorption energy was explicitly converged with respect to plane waves and k-point sampling until the variation with respect to these parameters was less than 0.01 eV/adsorbate. This required plane-wave cutoff equal to 400 eV and 4×4×1 k-point grid. Energy of In adatom in gaseous form was calculated using same parameters in 15×15×15 Å simulation box. Considering size and periodic boundary conditions of simulation cell, calculated coverages varied from 0.125 (1 adatom in cell) to 1.75 (14 adatoms in cell) ML with step of 0.125 monolayers. The slabs at all coverages were separated by at least 20 Å of vacuum space.

Of the 3 possible positions for the adatom adsorption shown in Fig. 1, *a*, there were 2 likely candidates – P1 and P3. At 0.125 ML coverage these systems showed very close total free energies of –735.95 eV and –735.83 eV, respectively (P2 had $E_{tot} = -731.58$ eV). When compared to higher coverages (0.375 ML), position 1 showed 0.48 eV lower energy than position 3. This is



the reason why P1 was chosen as main adsorption site over P3, which was initially expected to be preferred since it is a continuation of the metallic sublattice of Ga.

We calculate the absolute adsorption energy E_{ads}^{abs} which describes change in total energy of system induced by wetting layer as a whole. It is calculated independently at each coverage and then is divided by the number of adatoms forming wetting layer giving us averaged bonding energy of adatoms forming wetting layer at every coverage.

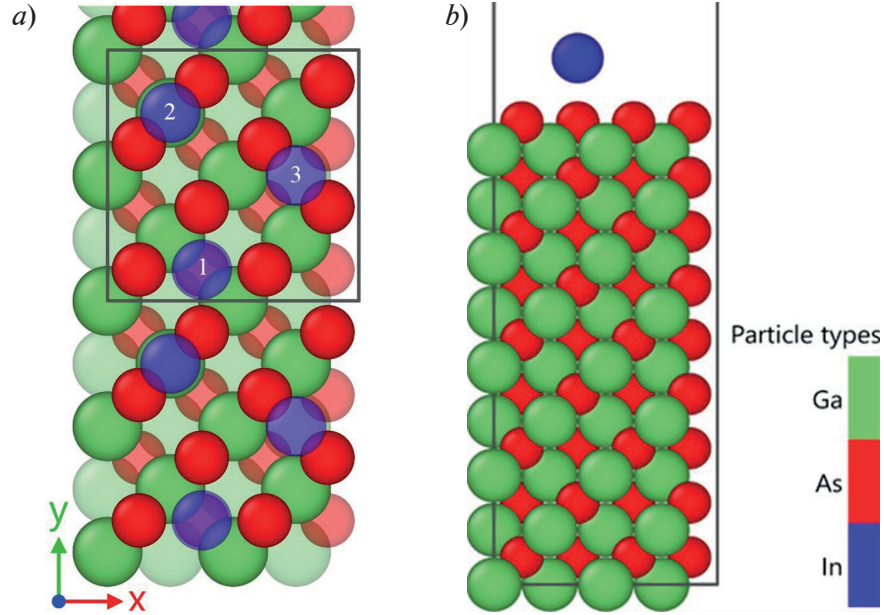


Fig. 1. Top view of the supercell replicated in the y direction showing possible adsorption sites (a) and side view of supercell (b)

Formula for absolute adsorption energy per adsorbate atom:

$$E_{ads}^{abs} = -(E_{GaAs+In} - E_{GaAsclean} - E_{In} \cdot N) / N \quad (1)$$

where $E_{GaAsclean}$ is the total free energy of the pristine GaAs surface, E_{In} – the energy of the In atom in gaseous form, N – number of adatoms forming wetting layer at given coverage (e.g., 4 adatoms at 0.5 ML coverage and 8 adatoms at 1 ML coverage) and $E_{GaAs+In}$ is the energy of the reconstructed surface with adatoms at given coverage. In this formula, a positive value of the adsorption energy correlates with a stronger interaction between the adatoms and the substrate.

We also calculate the relative adsorption energy – E_{ads}^{rel} value of which represents change in total energy of the simulated system cell induced by “single” adatom bonding with the surface. It is dependent on surface energy of system at previous coverage step, meaning that $E_{GaAsclean}$ from formula 1 is replaced by the energy of previous system, so for E_{ads}^{rel} at x ML coverage (where x is coverage of current system and $x-1$ is coverage of previous system) formula (1) changes into (2).

$$E_{ads}^{rel} \text{ at } x \text{ ML} = -(E_{GaAs+xIn} - E_{GaAs+(x-1)In} - E_{In}) \quad (2)$$

Also, since for our calculations of E_{ads}^{rel} we decide coverage step to be 0.125 ML (single adatom in simulation cell), there is no need to normalize our results as we did for E_{ads}^{abs} .

For E_{ads}^{rel} at 0.125 ML which is basically the same as E_{ads}^{abs} at 0.125 ML and inevitably includes a large energy change caused by the surface reconstruction (Fig. 2), we decided to calculate its value differently to get rough approximation of bond strength without reconstruction contribution. To do that in place of $E_{GaAs+(x-1)In}$ (which in this case is equal to $E_{GaAsclean}$) we used separately calculated energy of GaAs surface reconstruction at 0.125 ML coverage without the adatoms that caused the indicated reconstruction.

Results and Discussion

We start with the review of E_{ads}^{abs} curve, which shows a clear tendency for the adsorption energy to decrease with the growth of wetting layer. E_{ads}^{abs} gradually decreases nonlinearly

from 8.478 eV to 3.588 eV with the largest decrease occurring between 0.125 ML and 1 ML. At 1.75 ML coverage, this process almost completely stops with $\Delta E_{ads} < 0.01$ eV. The value at which E_{ads}_{abs} stops decreasing is close to the average E_{ads}_{rel} , which shows that the initial high value of the adsorption energy is distributed among all adatoms as wetting layer is formed. The most obvious reason why the first values of E_{ads}_{abs} are so high is that the reconstruction caused by first adatom is significantly more energy efficient than a clean surface of GaAs. This energy difference is part of E_{ads}_{abs} and affects all of its calculated values but loses its significance at higher coverages where adatoms start to form bonds with each other averaging the reconstruction effect.

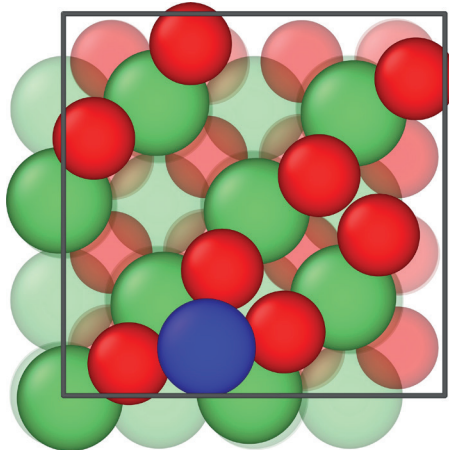


Fig. 2. Induced surface relaxation at 0.125 ML coverage

E_{ads}_{rel} roughly shows that the energy of bonds formed by individual adatoms varies depending on the position of bonding. Adatoms at coverages of 0.125 to 0.5 ML formed one symmetrical rectangular cluster on the substrate surface and had similar adsorption energies. While at 0.5 to 0.75 ML adatoms had to take positions between formed clusters and showed a decrease in bonding energy, adatoms that completed the full monolayer (0.75 – 1 ML) significantly increased E_{ads} , relieving the strain caused by the previous unstable configuration. This dependence of energy on the position and coverage is preserved in the second growing layer.

Other possible reasons for this change in adsorption energy include the bonds formation between surface adatoms and the modification of the electronic structure of the surface, which leads to the formation of antibonding states in the d-band [9]. Determination of the degree of influence of these factors on the adsorption energy requires additional studies.

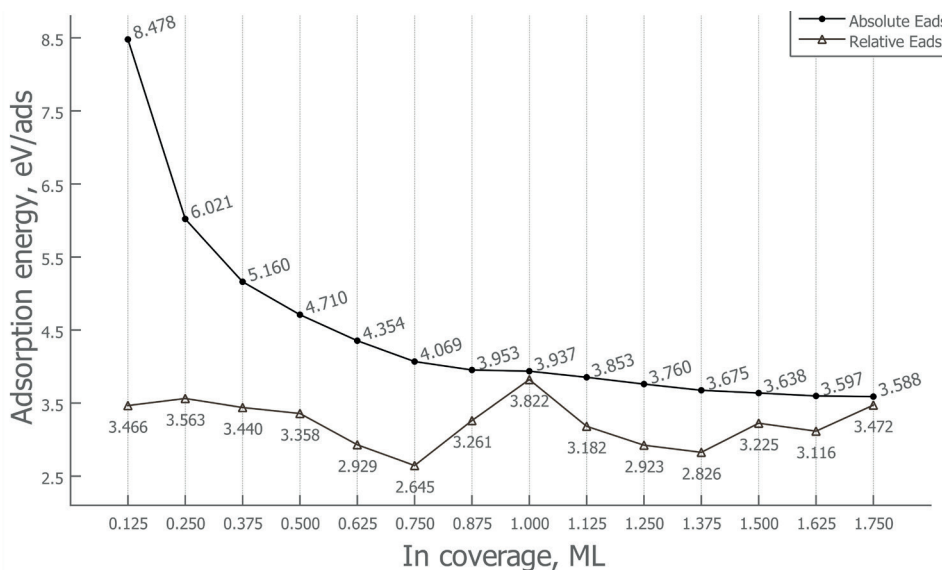


Fig. 3. Absolute and relative adsorption energy of In on GaAs depending on coverage



Conclusion

The demonstrated dependence of the adsorption energy on the coverage reduces the critical thickness of the wetting layer and leads to an increase in the rates of surface diffusion of adatoms after the formation of the initial wetting layer. This is expected to affect the formation of nanodroplets, increasing their size and decreasing their density. Further study of the mechanisms that cause these effects will allow us to better control the distribution and quality of quantum dots.

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