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Ab initio study of the nitridation of the GaAs (100) surfaces

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Abstract

We present, in this work, our preliminary results of a systematic theoretical study of the adsorption of N over As-terminated GaAs (100) (2×1) surfaces. We analyzed the changes in the bond-lenghts, bond-angles and the energetics involved before and after deposition. Our results show that the N-atoms will prefer the unoccupied sites of the surface, close to the As dimer. The presence of the N pushes the As dimer out of the surface, leading to the anion exchange between the N and As atoms. Based on our results, we discussed about the kinetics of the N island formation during epitaxial growth of the III-Nitrides.

Keywords: Surfaces; Adsorption; Total energy; Nitridation; III-Nitrides

1. Introduction

During the last decade, the group III-nitrides (AlN, GaN, InN) and the corresponding alloys have attracted great interest due to their succesful applications in the electronic and optoelectronic device technology [1]. However, their growth in the zincblende structure has been a hard task to the experimentalists, once the most stable structure for these compounds is the wurtzite one [2]. A lot of substrates has been proposed for the III-nitride growth in the cubic modification, and the nitridation of either SiC or GaAs surfaces seems to be the most efficient technique for such growth [3,4].

In order to understand the mechanisms for III-nitride growth in the zincblende structure based on the nitridation of GaAs (100) surfaces, we present, in this work, our preliminary results of a systematic theoretical study of the adsorption of N over As-rich GaAs (100) (2×1) surfaces based both on self-consistent total energy and force calculations, by using the density functional theory (DFT) in the local-density approximation (LDA) for the exchange-correlation term, within the plane-wave pseudopotential method [5], and on a kinetic Monte Carlo simulation of the epitaxial growth, based on the solid-on-solid approach [6].

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For the total energy calculations, we have used the Troullier-Martins pseudopotentials [7], and we have included Ga-3d electrons as valence states. The slab supercells used were build up of 5 atomic layers and a vacuum region equivalent of 5 atomic layers. We followed exactly as done in our previous work on (110) GaAs surfaces [8]. The calculated total energies were used as transition rates for the kinetic processes in our Monte Carlo simulation. We also have analyzed the changes in the bond-lengths and in the bond-angles before and after deposition, as well as the total energy behaviour of the adsorbate during this process.

2. Bulk equilibrium properties

Before to proceed the slab supercell calculations, we have evaluated the total energy for various values of the lattice constant in order to have a good description of the equilibrium properties of the bulk GaAs. The results were fitted by the Murnaghan equation of state, and we have obtained 5.63 (5.33) Å and 0.75 (0.75) Mbar, respectively, for the equilibrium values of the lattice parameter (a_0) and Bulk Modulus (B_0), when including the Ga-3d (or without the 3d electrons) in the calculations. Our results are in good agreement with the available experimental results [9]. The results were converged with a cutoff energy of 140 (80) Ry of the plane-wave expansion of the wavefunction, and a (4 4 4) Monkhorst-Pack mesh to sample the Brillouin zone, corresponding to 10 **k** special points were also used.

Table 1
Calculated structural parameters, as defined in Fig. 1, for the GaAs (100) (2×1) surfaces

Surface	α (degrees)	ω (degrees)	d_1 (Å)	d_2 (Å)	d_3 (Å)	d_1 (exp)(Å)
Ga-terminated	127.7	22.9	2.38	2.39	2.47	–
As-terminated	101.6	0	2.46	2.33	2.33	2.2–2.73

3. GaAs (100) (2×1) surfaces

While the As-terminated GaAs (100) surfaces are stable in a β2 (2×4) reconstruction pattern, the (2×1) surfaces were chosen for our simulations because, during the conditions of the GaN growth on GaAs substrates, i.e., at 700 °C, the GaAs (100) surface makes a phase transition to this reconstruction pattern [10]. So, before we start our adsorption simulation, we have studied the (2×1) reconstruction of both the Ga and As dimers over the GaAs (100) surfaces within the slab supercell model. In our calculations, the force were converged to 1 mHartree/Bohr.

In Table 1 we display the structural parameters for the two reconstructed surfaces as defined in Fig. 1. Our results agree well with the available experimental data, whenever these comparison is possible. It is interesting to note that, while the Ga-terminated surfaces have buckled Ga dimers, tilted by almost 23 degrees, the As terminated surfaces are formed by unbuckled dimers. We would like to mention that in the β2 (2×4) reconstruction pattern, the As dimers are slightly buckled ($\omega \sim 0.5$ degrees) [11]

4. N adsorption and diffusion

In Fig. 3, we show our preliminary results for the N adsorption for the sites described in Fig. 2. It is clear that the N-atoms will prefer the sites C, D and E, respectively, which are the unoccupied sites of the surface, before the surfactant effect between the N and As atoms occurs [4]. It is interesting to note that the adsorption over the As dimer (at the A site) is 1.48 eV less stable than that over the C site, which has an adsorption energy of 3.17 eV. Also, the adsorption at D and E sites are 1.09 and 1.12 eV less stable

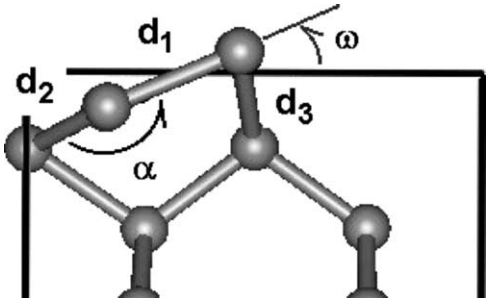

Fig. 1. Perspective view of the structural parameters which describes the atomic geometry of the GaAs (100) (2×1) surfaces.

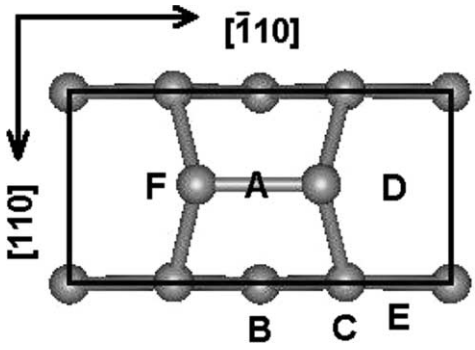

Fig. 2. Top view of the possible N adsorption sites over As-terminated GaAs (100) (2×1) surfaces.

than at the C site, respectively. We noticed that, unlike what it was observed for the N adsorption over GaAs (110) surfaces [8], there is no activation barrier for N before the beginning of the adsorption process.

In Table 2 we display the structural parameters for relaxation of the system after the N adsorption at C, D and E, as defined in Fig. 1. From the obtained results, we note that, only at the E site there was a slight distortion on the α angle towards to a planar configuration of As bonds. Also, only at the C site we detected a tilt of the As dimer, caused by the presence of N and, except for the adsorption at D site, the N prefers to stay close to the Ga atoms. In order to understand the changes of the bond lengths and bond angles, we depict in Fig. 4, the relaxed atomic positions after the N adsorption at the C site. It interesting to observe that the adsorbed N, in order to stay close to Ga atoms, distorts the As dimers, pushing them away from the surface. Based on our results, we suppose that, if another N atom comes, the anion exchange between As and N atoms begins,

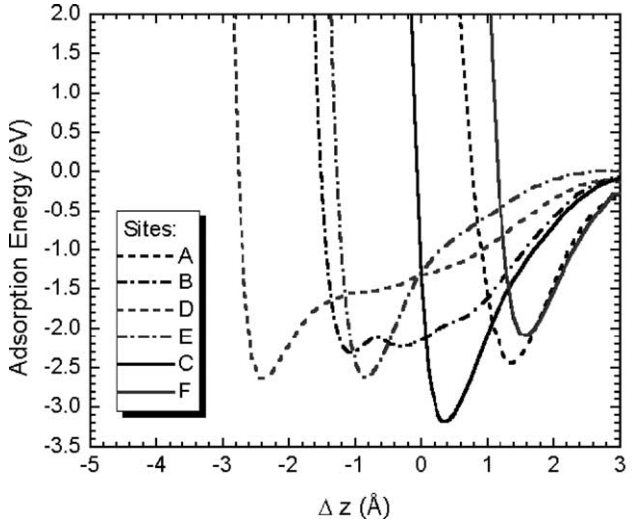

Fig. 3. Adsorption energy variation as a function of the height Δz (in Å) of the N adsorbed over the GaAs (100) (2×1) surface at the sites A, B, C, D, E and F, as defined in Fig. 2.