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Formation energies and abundances of intrinsic point defects at the GaAs/AlAs(100) interface

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Formation energies and electronic structures of all intrinsic point defects on quasi-T_d sites at the GaAs/AlAs(100) interface were calculated as a function of the chemical potentials of the electrons and atoms using density-functional theory. The results show that Al_{Ga} and Ga_{Al} will always be present in significant concentrations. Furthermore, we find that under As-rich conditions the cation vacancies and the anion antisite defects can occur in significant concentrations, whereas under As-poor conditions the cation antisites, cation interstitials and anion vacancies will play an important role.

The atomic-scale roughness as well as the stability of GaAs/AlAs interfaces and superlattices have been subject of several recent experimental studies [1–5]. It is well known that the quality of the interface of AlAs grown on GaAs is usually better than that of the interface of GaAs grown on AlAs. A thorough understanding of this effect is, however, not yet developed. The origin of the difference of the two differently prepared interfaces will partly be due to a different surface diffusion of Ga or As on AlAs compared to Al or As on GaAs. Another reason lies in the different Gibbs free energies of formation of intrinsic defects. In this paper we deal with the latter aspect. We identify the most important interface defects considering tetrahedrally coordinated intrinsic point defects in GaAs, AlAs and at the GaAs/AlAs(100) interface in dependence of the Fermi level position and of atomic reservoirs.

Our calculations are performed using density-functional theory and the local-density approximation for the exchange-correlation functional [6,7]. The ionic potentials are treated in the pseudopotential formalism where we use fully separable Kleinman–Bylander type pseudopotentials [8,9]. The k-integrals are approximated by using the Γ-point of our large supercell. We model the interface in a 108-atom cell, which contains three double layers of GaAs and AlAs. For this supercell the two interfaces can be considered as being decoupled, which was carefully checked by comparing charge densities and potentials of the superlattice and pure GaAs and AlAs crystals. All atoms are taken at the perfect zinc-blende positions with a lattice parameter equal to the mean value of those of GaAs and AlAs. The basis consists of plane waves with an energy cut off of 8 Ry. Instead of a matrix diagonalization technique we use the molecular-dynamical method of Car and Parrinello to minimize the total energy of the system [10].

In this set-up we calculated electronic structure and total energies for all intrinsic defects on quasi-T_d sites at the GaAs/AlAs(100) interface. We call the symmetry of these sites "quasi-T_d" because the full tetrahedral symmetry is of course broken at the interface. Nevertheless, the difference between Ga and Al atoms is not dramatic and interface defects will experience a (slightly) perturbed tetrahedral environment. Lattice relaxation was not taken into account. Based on the experience with substitutional defects in bulk GaAs (see e.g. ref. [11]) and assuming that only breathing relaxation would occur, we expect that

the energy gain due to lattice relaxation will be less than 0.5 eV. This would not alter our conclusions discussed below. For interstitials other distortions are possible. Therefore for these defects a more pronounced lattice relaxation energy gain may occur.

The formation energy of a defect that can occur in different charge states n, in dependence of the chemical potential for the electrons E_F, and the chemical potentials of the atoms μ_i is given by:

$$\Delta E(\mu_i, E_F) = \min\left[\Delta E(n) + E_F n\right]_n$$
$$+ \sum_i \mu_i \, \Delta N_i,$$

where ΔN_i is the particle-number difference of species i. The contributions of vibrational and electron–hole pair entropy to the Gibbs free energy were neglected since at normal temperature they contribute ≤ 0.2 eV for the studied systems [11]. We take into account that the atoms involved in the defect creation will come from or go to their atomic reservoirs. During growth or annealing the reservoirs for the atoms might be As_2 gas, Ga or Al metal or GaAs and AlAs bulk, and the reactions of the atoms with these reservoirs have to be taken into account, if one wants to get insight in the formation probability of different defects under different conditions. In order to explain how we obtained the results shown in figs. 1 and 2, let us describe the procedure for the gallium vacancy.

In a first step we simply take the Ga atom out of the crystal and bring it to infinity. In a second step we consider the two extremal cases of (1) a As_2 gas environment of the crystal and (2) Ga-rich conditions where Ga metal droplets are present. For the first case the Ga chemical potential is defined by the following reactions:

$$\tfrac{1}{2}As_2 \rightleftharpoons As,$$
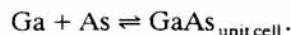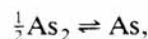
$$Ga + As \rightleftharpoons GaAs_{\text{unit cell}}.$$

The dissociation of the As_2 molecule costs 2.0 eV per atom [12] and the creation of a new GaAs unit cell brings an energy gain of 6.7 eV per atom [12]. So the net reaction energy – or the Ga chemical potential – under As-rich conditions is 4.7 eV. The reaction in case (2) is:

$$Ga \rightleftharpoons Ga_{\text{metal}},$$

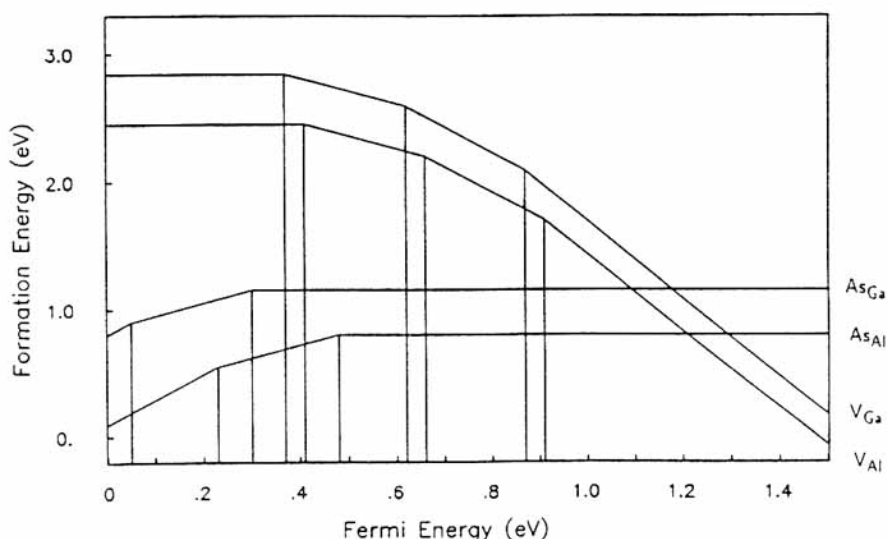which corresponds to a Ga chemical potential of 2.8 eV [12]. Depending on the partial pressures,

Fig. 1. Formation energies of intrinsic point defects at the GaAs/AlAs(100) interface in As-rich material as function of the Fermi energy. All other quasi-T_d symmetric point defects have higher formation energies.

experimental conditions lie within these two extremal cases. For the other defects the reactions are different, but our treatment for them is fully analogous [13].

The resulting formation energies for the dominating point defects at the interface are shown in fig. 1 for an As-rich environment. For As interstitials the formation energy is outside the energy range of the figure. Thus, these defects should not be important. The results of fig. 1 clearly show that in n-type material the cation vacancies dominate whereas in p-type material As antisites are more abundant. For a given temperature and in the limit of low concentrations one can assume that the defect concentrations obey an Arrhenius type of behaviour which means that the logarithms of the concentrations are proportional to the formation energies. This assumption of course breaks down for very small or negative formation energies, where the defect–defect interaction – especially when the defects are charged – leads to a saturation of the defect concentration. In As-poor material (cf. fig. 2) the cation antisites should be important. Only in strongly p-type material cation interstitials and the As vacancy become of some importance, although the overall concentration of intrinsic defects under these conditions should be relatively low. From the results of figs. 1 and 2 we can also determine the energies of defect–defect reactions which would not involve the above mentioned atomic reservoirs. These results will be published elsewhere; we note that these reaction energies compare well with those of self-consistent Green-function calculations of defects in bulk GaAs by Baraff and Schlüter [14].

All these formation energies will be relevant if the interface is in thermodynamic contact with the considered reservoirs. It should be noted that in full thermodynamic equilibrium the defects will not necessarily stay at the interface but will diffuse into the crystal bulk if this is energetically favourable. In fact, the defect formation energies of most of the considered defects are lower in the GaAs region than at the interface and higher in the AlAs region. This leads to a gradient of increasing defect concentration from AlAs to the interface to GaAs in thermodynamical equilibrium. The only exception is the As_{Al} in p-type material and in As-rich environment. One has to keep in mind that the defect diffusion can and will most probably be kinetically hindered so that the full thermodynamical equilibrium will not in all cases be achieved, but this is beyond the scope
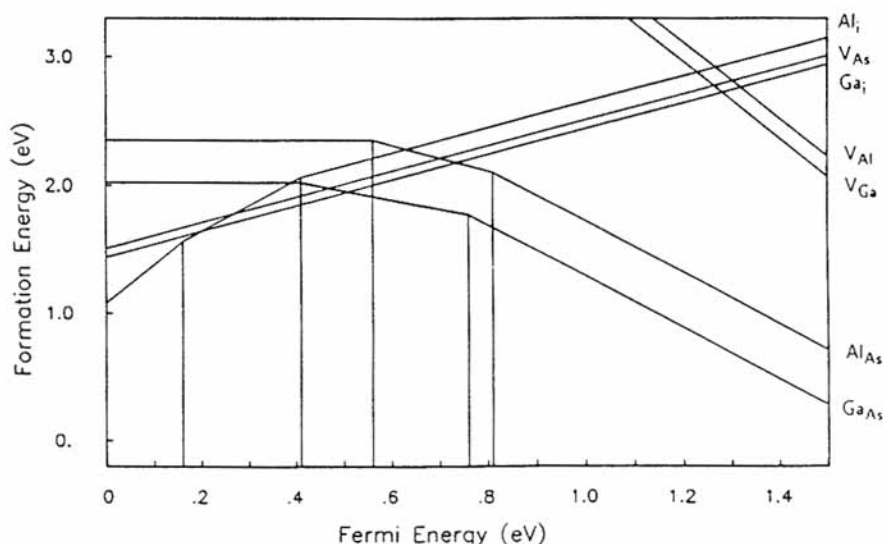

Fig. 2. As fig. 1 but for As-poor environment.

of our study. Finally we would like to mention a further possibility of interface-defect formation that shall be illustrated again for the case of the vacancy. Due to the presence of the interface a Ga vacancy can not only be formed by the Ga atom leaving the crystal and reacting with its reservoir but it can as well happen that the Ga atom occupies an Al site and the kicked out Al atom reacts with its reservoir. Instead of

$$0 \rightleftharpoons V_{Ga} + Ga_{reservoir},$$
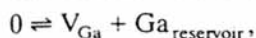
the reaction then writes

$$0 \rightleftharpoons V_{Ga} + Ga_{Al} + Al_{reservoir},$$

and in this case the second reaction is energetically favourable by 0.25 eV in As-rich environment. For all other defects one has to consider analogous reactions. The important difference to the above discussed mechanism is that now two defects are formed simultaneously. We find that under As-rich conditions V_{Ga} and As_{Ga} will be formed together with Ga_{Al} whereas under As-poor conditions Ga_{As} and Ga_i will be formed together with Al_{Ga}. Further details will be published elsewhere.

In summary using density-functional theory we calculated total energies for all intrinsic defects on quasi-T_d sites in GaAs, AlAs and at the GaAs/AlAs(100) interface in dependence of the chemical potentials for the electrons and atoms. Only in semi-insulating material and As-poor environment we find the overall concentration of intrinsic defects to be relatively small. In the other extremal cases antisite defects and cation vacancies are found to be the most abundant defects. It is likely that the defect concentration at the surfaces or interfaces is higher than in the bulk because at the surface thermodynamical equilibrium with the environment can be achieved

more easily, because of the mentioned defect-pair formation, and because the diffusion of interface defects into the bulk may be kinetically hindered. Due to the formation of Al_{Ga} and Ga_{Al} but also due to the formation of other defect pairs (for example V_{Ga} plus Ga_{Al}) at the interface, the GaAs/AlAs interface cannot be expected to be sharp on an atomic scale.

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