GaP/Si(100) is considered as pseudomorphic virtual substrate for III/V-on-Si integration in order to reduce defects related to polar-on-nonpolar heteroepitaxy. The atomic structure of the GaP/Si(100) heterointerface is decisive to yield low defect densities and its dependence on nucleation conditions is still under debate. Recently, Beyer et al. suggested the formation of a 'pyramidal' structure as a general mechanism at polar-on-nonpolar interfaces [A. Beyer et al., Chem. Mat. 28, 3265 (2016)]. However, their DFT studies neglected the dependence of the calculated interfacial energies on appropriate chemical potentials and their findings are contradictory to recent and past experimental data.

Recently, Beyer et al. reported on 'pyramidal' structure formation at the GaP/Si(001) heterointerface during low-temperature nucleation. As a key element of the results, a 'pyramidal' structure formation is suggested to be a general mechanism at polar-on-nonpolar interfaces, which would severely impact the interfacial electronic structure and technical feasibility of nano-dimensioned devices. This generalization, though, is not justified in the article at any point. As a second key element, the authors found abrupt Ga-terminated GaP/Si(100) interfaces to be more stable compared to P-terminated ones. These findings were deduced from experimental scanning transmission microscopy (STEM) high angle annular dark field (HAADF) images depending on quantitative modeling of the data and theoretical modeling including DFT calculations. They are in contradiction to experimental facts that have been published recently and also to recent theoretical calculations. In addition, the DFT studies in Ref. erroneously neglected the dependence of the calculated interfacial energies on appropriate chemical potentials.

The suggested (112) faceted interface model discussed in Ref. requires an equal number of Si–Ga and Si–P bonds, which is beneficial with respect to charge neutrality at the heterointerface. However, applying X-ray photoelectron spectroscopy, it was clearly shown quantitatively that Si–Ga bonds do not at all account for 50% of the interfacial bonds (for GaP nucleation in P-rich conditions). This experimental fact is not considered adequately by the authors. Another experimental observation is low energy electron diffraction patterns showing the ideal GaP(001)-(2×2)/c(4×2) surface reconstruction after only a few (TBP,TEGa) pulse pairs—equivalent to ca. 3 monolayers of GaP—without any indications of faceting.

With regard to the interfacial structure, it was shown that the sublattice orientation of the GaP epilayers can be controlled and inverted in dependence of (i) the amount of Ga available in the reactor (both with theoretical arguments and experimental evidence) or also (ii) by a rotation of the prevailing Si dimer orientation prior to GaP nucleation. It remains unclear how this could be achieved with the discussed 'pyramidal' interface structure. Also, it is not discussed how the step structure at the Si(001) surface can be preserved during atomic exchange, where Si atoms are assumed to be replaced across several monolayers, and how the domain structure of the Si(001) surface prior GaP nucleation corresponds to the amount of antiphase disorder induced into the GaP epilayer at the heterointerface. This correlation, however, is an experimental fact observed also by the very same group.

It should be noted, that the exact Si(001) surfaces discussed in Ref. are more sensitive to the formation of elongated vacancy islands on the terraces due to etching of Si by interaction with the H2 ambient as shown in Ref. [8]. Vacancies induce depression on the terraces in the range of one to few monolayers of Si, which causes additional anti-phase disorder. The scanning tunneling microscopy (STM) measurements in Fig. S1 in the supplementary material of Ref. show the presence of multiple vacancy islands on their terraces and only single atomic steps. The authors do not comment on the significant occurrence of these vacancy islands. Their evolution has already been thoroughly described in Ref. [8] and could also be an origin of three-dimensional structures obtained in the STEM analysis of Ref. [1].

Theoretical investigations of Beyer et. al revealed that the abrupt Si-Ga interface is energetically more favorable than the Si-P interface. This conclusion contradicts experimental and theoretical results in literature. While relative interface formation energies were used in Ref. [8], Beyer et al. have computed absolute interface formation energies of various GaP facets. The interface energy for superlattices was defined as

\[ \Delta E_{if} = \frac{1}{2}(E_{Si} + E_{GaP}) - E_{GaP/Si}/A , \]  

(1)
where $E_{Si}$ and $E_{GaP}$ are the total energy of the Si and GaP slabs, $E_{GaP/Sl}$ is the total energy of the slab of the entire heterostructure, and $A$ is the area of the cell (which is assumed unity for the $(1 \times 1)$ cell in the following). Superlattices, however, consist of two interfaces with both polarities and, therefore, the absolute interface energy of a single interface cannot be derived by eq. (1) but only the sum of two interface energies. The absolute energies were computed from slab calculations in Ref. [1]. In the following, we will demonstrate that eq. (1) is not really valid for slab calculations.

In Fig. 1 (a) and (b), slabs with even and odd numbers of layers, respectively, of Si and GaP layers are shown. The employed slab configuration consists of GaP layers, Si layers, surfaces and interfaces with altogether 16 layers (Fig. 6 in Ref. [1]). The total energies of Si and GaP slabs have the following contributions:

$$E_{Si} = E_{Si}^{bulk} + 2E_{Si-H}$$

$$E_{GaP} = E_{GaP}^{bulk} + E_{Ga-H} + E_{P-H}$$

where $E_{Si-H}$, $E_{Ga-H}$, and $E_{P-H}$ are the corresponding surface energies and $E_{Si}^{bulk}$, $E_{GaP}^{bulk}$ are the bulk energies, i.e. the energies of the 16 Si resp. GaP bilayers in the slabs. For the slab with Ga-Si interface, the total energy can be expressed as

$$E_{GaP/Sl} = E_{Si-H} + (E_{Si}^{bulk} + E_{GaP}^{bulk})/2 + E_{Ga-Si} + E_{P-H}$$

where $E_{Ga-Si}$ is the Ga-Si absolute interface energy. By substituting eq. (2), eq. (3) and eq. (4) in eq. (1), the bulk and the Si-H surface energies are annihilated—but the surface energies $E_{Ga-H}$ and $E_{P-H}$ are not. In consequence, the interface energy can be expressed as

$$E_{Ga-Si} = \alpha - \Delta E_{if}$$

$$E_{P-Si} = -\alpha - \Delta E_{if}$$

$$\alpha = 1/2(E_{Ga-H} - E_{P-H})$$

Therefore, the $\Delta E_{if}$ defined in Ref. [1] is not the absolute interface energy. It involves the surface energy contributions from two H-terminated surfaces. $\alpha$ depends on the type of surface reconstruction (termination by H or pseudo H, for instance) and on the type of surface facet. It is obvious, that the surface energy of various facets depends on the chemical potentials $\mu_{Ga}$, $\mu_{P}$, and $\mu_{H}$. Surface energies and $\alpha$ can be derived for polar semiconductors. It is important, however, that $\alpha$ depends on the chemical potentials $\mu_{Ga}$, $\mu_{P}$, and $\mu_{H}$ and, therefore, the interface energy derived from slab calculations with even numbers of layers will also depend on the chemical potential. This is not discussed by Beyer et al. at all. The implicit assumption that $\alpha = 0$ for even slabs, i.e. $E_{Ga-H} = E_{P-H}$ for all facets of the GaP crystal is hard to be rationalized and can lead to misleading conclusions about the interface stability.

Surface energy contributions can be avoided by using slabs with odd numbers of layers, i.e. with an additional Ga layer for one type of the heterostructure [Fig. 1 (b)]. In this case, eq. (3) becomes

$$E_{GaP} = E_{GaP}^{bulk} + 2E_{Ga-H} + E_{Ga}$$

where $E_{Ga}$ is the energy of additional Ga layer in GaP bulk. It can be expressed by chemical potentials. In thermodynamic equilibrium, the chemical potentials are equal to the bulk chemical potentials. In the particular case discussed here, it holds $E_{Ga} = \mu_{Ga}$. By substituting eq. (5) and eq. (2) into eq. (1), one then obtains the following expressions:

$$E_{Ga-Si} = \alpha - \Delta E_{if}$$

$$E_{P-Si} = -\alpha - \Delta E_{if}$$

$$\alpha = 1/2\mu_{Ga}$$

Similarly to the even case in Fig. 1 (a), the interface energy depends on the chemical potentials and it is expected to be different for various facets of the GaP crystal.

Hence, it is important to consider the appropriate chemical potentials in the DFT calculation of interface.

FIG. 1. Schematic of GaP/Si slabs with (a) even and (b) odd numbers of layers. In (a), slabs consist of 8 (16) GaP (grey) resp. Si bilayers (green), one P-H (red), one Ga-H (blue) and one Si-H (light blue) surface, as well as one Si-Ga (cyan) or Si-P (orange) interface. In (b), the slabs contain an additional Ga layer.
energies and, in particular for even slabs, to involve the surface energy contributions in order to get correct values.

One reason for the discrepancy in the experimental findings in Ref. [1] and the observations in literature could originate in the highly non-equilibrium surface and interface preparation in metalorganic vapor phase epitaxy, which is sensitive to smallest disturbances as well as to the history of the growth reactor. Processes in Refs. [2, 3, 6, 8, and 12] were therefore established with continuous in situ control by reflection anisotropy spectroscopy.

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1 A. Beyer, A. Stegmüller, J. O. Oelerich, K. Jandieri, K. Werner, G. Mette, W. Stolz, S. D. Baranovskii, R. Toner, and K. Volz, Chem. Mat. 28, 3265 (2016).
2 O. Supplie, M. M. May, G. Steinbach, O. Romanyuk, F. Grosse, A. Nägelein, P. Kleinschmidt, S. Brückner, and T. Hannappel, J. Phys. Chem. Lett. 6, 464 (2015).
3 O. Supplie, S. Brückner, O. Romanyuk, H. Dösscher, C. Höhn, M. M. May, P. Kleinschmidt, F. Grosse, and T. Hannappel, Phys. Rev. B 90, 235301 (2014).
4 G. Steinbach, M. Schreiber, and S. Gemming, Nanosci. Nanotechnol. Lett. 5, 73 (2013).
5 P. H. Hahn, W. G. Schmidt, F. Bechstedt, O. Pulci, and R. del Sole, Phys. Rev. B 68, 033311 (2003).
6 O. Supplie, M. M. May, C. Höhn, H. Stange, A. Müller, P. Kleinschmidt, S. Brückner, and T. Hannappel, ACS Appl. Mater. Interfaces 7, L9325 (2015).
7 H. Dösscher, T. Hannappel, B. Kunert, A. Beyer, K. Volz, and W. Stolz, Appl. Phys. Lett. 93, 172110 (2008).
8 S. Brückner, P. Kleinschmidt, O. Supplie, H. Dösscher, and T. Hannappel, New J. Phys. 15, 113049 (2013).
9 C. E. Dreyer, A. Janotti, and C. G. V. de Walle, Phys. Rev. B 89, 081305 (2014).
10 H. Li, L. Geelhaar, H. Riechert, and C. Draxl, Phys. Rev. Lett. 115, 085503 (2015).
11 O. Romanyuk, T. Hannappel, and F. Grosse, Phys. Rev. Lett. 88, 115312 (2013).
12 S. Brückner, H. Dösscher, P. Kleinschmidt, O. Supplie, A. Dobrich, and T. Hannappel, Phys. Rev. B 86, 195310 (2012).