Pyramidal Structure Formation at the Interface between III/V Semiconductors and Silicon

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Supporting Information

ABSTRACT: An enhancement of computer performance following Moore’s law requires the miniaturization of semiconductor devices. Presently, their dimensions reach the nanoscale. Interfaces between materials become increasingly important as the volume is reduced. It is shown here how a pyramidal interface structure is formed irrespective of the conditions applied during the growth of two semiconductors. This drastically changes the common view of interfaces, which were assumed to be either atomically abrupt or interdiffused. Especially in semiconductor heteroepitaxy, a simple surface segregation of one atomic species is often assumed. It is proven by first-principles computations and kinetic modeling that the atom mobility during growth and the chemical environment at the interface are the decisive factors in the formation of the actual structure. Gallium phosphide grown on silicon was chosen as representative, nearly unstrained material combination to study the fundamental parameters influencing the interface morphology. Beyond that, this system has significant impact for cutting-edge electronic and optoelectronic devices. The findings derived in this study can be generalized to aid the understanding of further relevant semiconductor interfaces. This knowledge is crucial to comprehend current and steer future properties of miniaturized devices.

1. INTRODUCTION

In semiconductor industry it is required to maximize the density of integrated circuits to continue the ongoing performance increase of microelectronic devices.1 Fundamental questions on how to achieve this are, as yet, unanswered and the “Red Brick Wall”—meaning necessary technological solutions not being found—is approaching. This industry is currently following two approaches to reach their performance goals: downscaling of device dimensions and extending beyond the state-of-the-art silicon (Si) complementary metal–oxide–semiconductor (CMOS) technology.1,2 Both approaches necessitate the development of new architectures and new materials. Downscaling, for example, requires new high-k compounds to prevent tunnelling processes.3 Progress beyond current CMOS technology, on the other hand, also needs materials that overcome silicon’s fundamental limitation of not enabling optical excitations due to an indirect band gap. So-called III/V semiconductors, mixtures of elements in the third and fifth main group of the periodic table, are highly promising, for example, for conducting channels4–9 or even laser applications.10,11 Monolithic integration of these materials with Si is desired to enable seamless integration with current CMOS technologies. This can be achieved with up-scalable growth techniques, specifically metal organic vapor phase epitaxy (MOVPE). However, the requirements regarding the quality (lack of defects) of the films deposited is very high, resulting in major experimental challenges.12 The difference in lattice constants and polarity between Si and III/V semiconductors leads to misfit dislocations, stacking faults, twins, and antiphase boundaries, which severely impedes the resulting device performance. In addition, thermal expansion coefficients of both materials differ, which results in cracking for thicker layer stacks. This can be avoided by using lattice-matched material combinations or strain-balancing at growth temperature.13 Deterioration of electronic properties via atoms moving into the neighboring material (cross-doping) also requires suitable growth conditions. On a microscopic level, it is usually assumed that the morphology and the defect structure of III/V layers grown on group IV (here: Si) substrates are mainly determined by the charge neutrality of the interface. This charge distribution is expected to be the outcome of carefully choosing the growth conditions.

One way of remedying several of the issues mentioned above is to provide an interlayer of gallium phosphide (GaP) between...
Si and the optically or electrically active III/V device. Gallium phosphide (GaP) is the only III/V semiconductor, which is nearly lattice-matched to Si at room temperature, with a remaining lattice mismatch of only 0.37%. This enables the defect-free growth of layers of several tens of nanometers thickness without reaching the critical thickness where defects would be formed. Moreover, by carefully tuning the growth conditions, an intact GaP layer can be produced even on CMOS-compatible exact Si(001) substrates. Nevertheless, as current device dimensions are decreased to end up in the range of interface widths, the exact interface morphology between Si and GaP plays an increasing role, and knowledge about the thermally stable, intrinsic configuration is needed to ensure optimal integration of the active III/V device. Therefore, quantitative understanding of the interface formation and structure has a direct impact on device performance. Furthermore, the exact interface structure between any two materials must be known to enable meaningful conclusions to be drawn regarding fundamental physical processes occurring across interfaces, such as charge or energy transfer. Although atomistic processes during material growth are well understood, our fundamental understanding of the formation mechanisms leading to certain buried interface structures is lacking behind.

Interfaces between III/V semiconductors, for example, accommodate small differences in lattice parameters by elastic deformation of one of the components. Especially for indium (In)- and antimony (Sb)-containing materials it is widely accepted that In or Sb, respectively, segregate toward the In- and antimony (Sb)-containing materials it is widely accepted,16 our fundamental understanding of the formation of atomistic processes during material growth are well under- stood,16 our fundamental understanding of the formation mechanisms leading to certain buried interface structures is lacking behind.

In this manuscript, we utilize atomic-resolution transmission electron microscopy combined with contrast modeling to reveal an unexpected, structured interface between GaP and Si. With the help of theoretical modeling by means of kinetic Monte Carlo (KMC) simulations, we show the kinetic pathway to the formation of this interface. Finally, we use density functional theory (DFT) to verify the assumptions made in the KMC simulations and explain the energetic preference of this structured, faceted interface compared to an abrupt, flat one.

2. EXPERIMENTAL SECTION

2.1. Growth Procedure. The GaP layers were grown on silicon substrates via MOVPE in an Aixtron AIX 200 GFR reactor. Prior to growth, a wet chemical etching procedure was applied to the exact Si(001) substrates. A homoepitaxial buffer was grown using silane as precursor. It has been verified by Scanning Tunneling Microscopy (STM) from samples transferred under vacuum that the terraces on the Si surfaces after this treatment and prior to GaP growth were atomically flat (see Figure S1). The Si surface after buffer layer growth is predominantly double-layer stepped with a terrace width of around 130 nm. There are some monatomic steps on this surface, but again, the terrace area is in the range of 100 × 100 nm². This is significantly larger than the area investigated in scanning transmission electron microscopy (STEM). Triethylgallium (TEGa) and tertiary-butylphosphine (TBP) were used as precursors for Ga and P, respectively. The optimized growth procedure consists of two steps. First, a nucleation layer is deposited typically at low temperatures, which already determines the interface structure. The thickness of the nucleation layer is in the range of 7–10 nm. Second, a high temperature overgrowth is applied to self-annihilate antiphase boundaries, which can originate at the monatomic steps mentioned above. As the overgrowth layer does not have any influence on the formation of the buried interface between GaP and Si, it is not further discussed here. To investigate the influence of the growth conditions of the nucleation layer on the interface structure, crucial parameters like temperature and preflow of the precursors and substrate off-cut were varied in separate samples. Though the temperature significantly influences the surface diffusion, the preflow can be used to influence which element bonds to the Si first, whereas the off-cut of the substrate determines the density of steps on the surface, which can significantly influence the growth kinetics. All nucleation layers were grown in pulsed mode, where the P and Ga precursor are offered sequentially. For the samples shown in the paper, two temperature regimes were investigated: low-temperature nucleation at 450 °C ("Exact", "2" off, "Reversed Polarity") and high temperature nucleation at 675 °C ("High temperature"). For the low temperature growth, the substrate off orientation was varied ("Exact" ⇔ "2" off). The element bonding to the Si first was changed to achieve both GaP polarities on the same Si surface ("Exact" ⇔ "Reversed Polarity"). This was achieved by applying the procedure described in ref 25.

2.2. STEM (Scanning Transmission Electron Microscopy) Characterization and Modeling. 2.2.1. TEM Sample Preparation. After the growth, electron transparent foils were prepared via conventional mechanical polishing followed by 5 keV argon ion milling from both sides with an angle of incidence of 4° in a Gatan precision ion polishing system. Final polishing was carried out at 1.7 keV to reduce the amount of amorphous material on the samples. The viewing direction was chosen along a ⟨110⟩ axis of the Si substrate. Before starting the STEM measurements, the samples were treated in a Fischione model 1020 plasma cleaner to remove residual hydrocarbon contaminations.

2.2.2. STEM Measurement. The HAADF (high angle annular dark field)-STEM measurements were carried out in a JEOL 2200 FS, operating at 200 kV, which is equipped with an aberration corrector for the probe forming lens system. The condenser aperture used results in a convergence semiangle of 24 mrad and the annular detector collects electrons scattered in the range between 43 and 173 mrad. The parameters of the amplifier, namely, brightness and contrast, were chosen in a way that neither low intensities are lost nor the detector is saturated at high intensities. A linear feedback behavior for the detector with respect to the incoming electron current was verified by varying the probe current by using different probe size settings and different condenser apertures sizes. Special care was taken that the investigated regions do not exhibit steps at the interface or antiphase domains (APDs) in the GaP, both of which could lead to a

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Here, we decided to use relative intensities instead, as they are intensity of the impinging beam, which can be facilitated via a detector simulations, the experimental data have to be normalized to the of the microscope used. In order to compare the experiments with The actual measured HAADF-intensity depends on the beam current neighbors or the background between the peak positions. The actual measured HAADF-intensity depends on the beam current, that is, the counts generated by the amplifier without electrons hitting the detector, is subtracted. The background noise can be determined by the acquisition of a STEM image with closed beam valve. The intensity on the atomic columns is predominantly determined by the chemical composition, whereas the region between the columns is also sensitive to effects of strain and disorder. The commercially available Peak Pairs software was used to determine the positions of the atomic columns with subpixel accuracy. Si as a group IV element can replace Ga as well as P. Therefore both columns in a dumbbell have to be evaluated separately in contrast to, for example, the AlAs/GaAs system where the dumbbell ratio can be used to evaluate the composition. To reduce the influence of experimental noise, for example, fly back errors during the scan process or uncertainties in determination of the peak positions, the intensity was averaged in a circular region around each peak position. The radius of integration was chosen as one-third of the next nearest distance, which turned out to be the optimum value for reduction of noise without introducing influences due to the neighboring peaks or the background between the peak positions. The actual measured HAADF-intensity depends on the beam current of the microscope used. In order to compare the experiments with simulations, the experimental data have to be normalized to the intensity of the impinging beam, which can be facilitated via a detector scan. Here, we decided to use relative intensities instead, as they are not sensitive to the used settings of the amplifier as long as one sticks to the linear regime. Therefore, the intensities measured in an image were normalized to the highest intensity, that is, the value for a pure Ga column. Ga has the highest atomic number of the three elements present.

### 2.2.4. Simulation of STEM Images

Complementary multislice simulations were performed using the HRTEM package in an absorptive potential approximation. The decisive parameters (residual aberrations, convergence angle, and detector range) were experimentally determined by the aberration corrector software and applying the procedure described in ref 30, respectively, and taken into account in the simulation. The sample thickness as well as the chemical composition were varied to investigate their influence on the HAADF intensity individually.

The data obtained, that is, the thickness—composition matrix (see Figure S2), served as a database for the comparison with experimental data. As a sanity check that the electron beam propagation and STEM contrast simulation does not influence the evaluation, a theoretically derived interface has been evaluated with the same procedure. The results are shown in Figure S3.

### 2.2.5. Density Functional Theory (DFT) Computations

Periodic DFT calculations were performed applying an exchange-correlation functional by Perdew, Becke, and Ernzerhof based on the generalized-gradient approximation (PBE) together with a semiempirical dispersion correction scheme (D3(BJ)). The approach chosen here represents the state-of-the-art methodology in computational material sciences and comparable methodology was found previously to be reliable for Si/GaP interfaces. The use of a projector-augmented wave formalism allowed the truncation of the plane-wave basis set at a kinetic energy cutoff of 400 eV. The Brillouin zone was sampled by \( \Gamma \)-centered k-meshes with \( 6 \times 12 \times 1 \) (hopping), \( 4 \times 4 \times 2 \) ((001) interfaces), \( 8 \times 4 \times 1 \) ((111) and (112) interfaces) k-points via the Monkhorst-Pack method. Spin polarization was considered in all calculations. The Vienna Ab Initio Simulation Package (VASP), version 5.3.5 was used. The total energy of the system was converged to \( 10^{-6} \) eV in every electronic relaxation step. Construction of all supercells was based on a silicon bulk cell with diamond structure using the experimental lattice
constant \((a = 5.431 \, \text{Å})\). For an estimation of strain due to the minimal lattice mismatch between Si and GaP, the supercells were elongated along the \(c\) axis, whereas in-plane lattice parameters were kept fixed (theoretical epitaxy, for more details see section 3.2 below).

The supercell for the adatom hopping barriers consisted of eight layers of silicon atoms representing the (001) surface model with an unreconstructed top layer and bottom layer saturated by hydrogen atoms. A vacuum region of 12.2 Å was added. This setup represents the model chosen in the subsequent KMC simulations. P-terminated surfaces were generated by substituting the top four layers of Si by alternating Ga and P layers (resulting in a \((\text{Si})_4 - \text{Ga} - \text{P} - \text{Ga} - \text{P}\) layer structure). Ga-terminated surfaces carried one more Ga-layer \((\text{Si})_4 - (\text{GaP})_2 - \text{Ga}\). No structural relaxation of the supercells was allowed. Minima and transition states were found via structural relaxation of the adatom positions until residual forces were converged to <0.01 eV/Å. Vibrational frequency calculations at the \(\Gamma\)-point were carried out via density functional perturbation theory \(^{44,45}\) to identify transition state structures that exhibit one imaginary mode in accordance with displacement patterns that prove they are part of the potential energy surface of the intended hopping movement. The transition states presented here connect two minima, whereas a complete hopping step ends at the translationally equivalent minimum position in a neighboring cell. As the adatom positions were not restricted to ideal lattice sites, this required two elementary steps for the Si and P adatoms but only one for Ga. However, the additional hopping barriers for Si and P are negligible compared to the rate-determining ones and are not shown for clarity. For the Si(001) surface, adatom hopping barriers were also determined for the well-known \((2 \times 1)\) dimer reconstruction applying six-layer substrate slabs in the frozen double-layer approximation (i.e., the top four layers of the slab were allowed to relax) in combination with the Nudged Elastic Band method. \(^{46}\) It is shown that the same trends \(\text{(P adatoms exhibit much larger hopping barriers than Ga and Si adatoms)}\) are derived with both models. \(^{44,45}\) Moreover, this interface region constitutes a peculiar morphology, as will be shown by quantitative analysis. The interface is neither atomically abrupt, nor does it have a purely interdiffused profile. It stretches over a region significantly wider than two monolayers, which is the expected roughness resulting from a charge neutrality interface model. \(^{37}\) Surprisingly, the interface region extends over several atomic layers. This intermixing of GaP and Si can also be observed in the thick sample’s composition map. However, projection effects tend to overlay the distinct pyramids more than in the thin sample, as their lateral size expands to only several nanometers. In the following, the terminology “intermixing” will be used for a structured interface only in order to discriminate this from a purely thermally interdiffused interface. At this point, it should be noted that the Si surface prior to GaP deposition was purely thermally interdiffused with the same degree of roughness. \(^{38}\)

3. RESULTS AND DISCUSSION

3.1. Quantification of the Chemical Composition and Morphology at the Interface. State-of-the-art aberration (probe)-corrected STEM, where electrons scattered from the specimen into high angles are collected by an annular detector (HAADF imaging), was applied to determine the chemical composition as well as the morphology of the GaP/Si intermixing region. The scattering contrast, which is proportional to the atomic number of the scatterer and also depends on the microscope settings and sample parameters, was simulated using an absorptive potential method. \(^{32}\) This approach yields a quantitative distribution of the elemental composition across the interface at atomic resolution. One can clearly resolve the individual atomic columns in the GaP layer and the Si substrate in the experimental HAADF images \((\text{Figure 1a,b})\). The Ga atom columns have the brightest contrast due to the largest atomic number, followed by the Si and P atoms. A thick (20 nm) TEM sample region is shown \((\text{Figure 1a})\) next to a thin (8 nm) TEM sample region \((\text{Figure 1b})\). This sample was nucleated at 450 °C in pulsed mode on exact Si (001) Si substrates depositing P as first element. The image shown in \((b)\) is an average of 40 individual images, which were aligned nonrigidly utilizing the Smart Align software. \(^{26}\) The micrographs for the two different thicknesses are shown \((a\) and \(b)\) because structured interface morphologies on a nanometer scale are potentially imperceptible in thick TEM samples due to projection effects. However, the thick TEM samples contain identical information on the interface morphology, as will be shown by quantitative analysis. Additionally, the samples were investigated in two perpendicular (110)-projections to be able to conclude on the three-dimensional structure of the interface.

The chemical composition on each atomic column was derived by quantitative modeling of the electron scattering, as described in the Experimental Section \((\text{see Figure S2 for the contrast simulation details})\). The Si occupancy of each atomic column across the interface is presented for the thick and thin sample regions in Figure 1c and d, respectively. The intermixing region between GaP and Si was found to exhibit a structure drastically different from the commonly assumed one: The interface is neither atomically abrupt, nor does it have a purely interdiffused profile. It stretches over a region significantly wider than two monolayers, which is the expected roughness resulting from a charge neutrality interface model. \(^{37}\) The intermixing of GaP and Si can also be observed in the thick sample’s composition map. However, projection effects tend to overlay the distinct pyramids more than in the thin sample, as their lateral size expands to only several nanometers. In the following, the terminology “intermixing” will be used for a structured interface only in order to discriminate this from a purely thermally interdiffused interface. At this point, it should be noted that the Si surface prior to GaP deposition was purely thermally interdiffused with the same degree of roughness. \(^{38}\)

The derived chemical composition maps \((\text{Figure 1c,d})\) were integrated laterally yielding the quantitative composition of elements across the interface, as depicted in Figure 2 \((\text{blue data represent the experiment, red and green data represent simulation results, as discussed later})\). Again, data from thick \((a)\) and thin \((b)\) sample regions are presented. The integration was carried out over the field of view shown in Figure 1, which consists of 38 \((a)\) and 76 atomic planes \((b)\) along the respective \((110)\) direction for the thick and thin sample. It is worth noting that integrating Figure 1b over 38 planes only, that is, the same width as \((a)\), leads to analogue results with a slightly increased standard deviation. Both images were acquired from the same sample and the evaluation results in an identical intermixing. This extends over about seven atomic layers. The intermixing zone is defined by taking the number of atomic layers, which exhibit a Si fraction between 10% and 90%. As expected, average intensities for the thick as well as the thin sample yield the same intermixing because we average over the structure of the interface. In order to assess a potentially structured interface, the quantitative composition profiles are provided next to the standard deviation (SD) of the composition along the integrated line scan. The SD is a measure of the nonhomogeneity of the intermixing, that is, the degree of structuring present at the interface. The SD is larger for the thin TEM sample, which confirms a structured interface morphology that is more eminent in TEM samples with thicknesses.
approaching the characteristic length of the structuring. Nevertheless, thick TEM samples equivalently contain all the information on the interface intermixing. To ensure that the different viewing directions for the thin (P-polar) and the thick (Ga-polar) sample do not influence the composition profiles, a thin sample in [110] projection was evaluated as well. The data are in agreement with the ones of the thin sample in [−110] projection (Figure 2b) and are shown in Figure S4. It is worth noting that the values of the standard deviation in Figure 2a,b are higher in the GaP side of the graph compared to the values in Si. This is caused by noise in the experimental data, which is higher for the GaP material, as we found the noise to be proportional to the HAADF intensity. The origin of this noise is most likely the amplifier of the used HAADF-detector. The analogue evaluations of simulated images, which do not suffer from this noise, do not show the increased SD in the III/V material as can be seen in Figure S3.

The MOVPE growth conditions of the GaP/Si heterostructure were varied over a wide range, as summarized in the Experimental Section, in order to separate extrinsic from intrinsic influences on the interface formation. The growth parameters were chosen and monitored with extreme care. Low growth temperatures were applied in order to allow intrinsic interface morphologies to form and prevent additional interdiffusion which can result from high temperature growth. The striking, structured morphology at the intermixing region between Si and GaP layers was observed for all growth conditions investigated at low growth temperature. High temperature growth can alter the morphology from intermixing to interdiffusion. Irrespective of the miscut of the substrate or the choice of the element first deposited in epitaxy, the highly unexpected structure features pyramidal shapes and intermixing over about seven monolayers at the GaP/Si interface. Integrated compositions (Si fraction) of GaP/Si interfaces grown under different conditions are compared in Figure 2c, the raw images and 2D evaluations can be found in Figure S6. The quantitative composition profiles of the samples grown at low temperature are equivalent, proving the characteristic interface morphologies are identical (7 layers intermixing with pyramids). This intrinsic interface morphology can only be changed by significantly increasing the growth temperature ("High temperature", blue data points in Figure 2c). As expected, a significantly wider, interdiffused interface with a width of 13 atomic layers is found for the high temperature growth conditions. The interdiffusion is then very homogeneous and no characteristic structuring is visible at the interface (the corresponding atomically resolved HAADF STEM image and its quantitative simulation are shown in Figure S5).

We conclude that the intrinsic GaP/Si interface is significantly wider and reveals more structural features than previously suggested morphologies derived from a simple model.47 The previous model considers charge neutrality at the interface and describes an extension of the interface of two monolayers. Moreover, no structured interfaces have been suggested so far. It is the aim of the theoretical modeling presented in the following to understand the physical origins of this interface geometry and whether there are thermodynamic or kinetic influences on the formation of this characteristic structure during the growth. The insights gained can be generalized toward the formation of other III/V–IV interfaces in semiconductor heteroepitaxy.

### 3.2. Computational Modeling

Computational modeling was performed in order to understand the experimental

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**Figure 2.** Silicon fraction on each atomic column and a measure of structuring (standard deviation of composition data in integration direction: SD) vs monolayers across the GaP/Si interface of the (a) thick (20 nm) and (b) thin (8 nm) TEM sample (blue) compared to the corresponding simulation results (red). The region of significant intermixing is indicated in the composition profiles in gray. Its width is defined by taking the number of atomic layers, which exhibit a Si fraction between 10% and 90%. The theoretical Si depth profile and clustering for the pure diffusion case is shown as the green curve in (a). In (c) integrated Si depth profiles across the GaP/Si interfaces are shown for the samples grown under the highly different conditions: green curve, nucleated in pulsed growth mode at 450 °C using P as first pulse on exact Si(001) substrates; red curve, nucleated in pulsed growth mode, first pulse of P at 675 °C to change the polarity, then cooled down to 450 °C to grow the remainder of the nucleation layer on exact Si (001) substrate; yellow curve, same nucleation conditions as green curve on 2°-off oriented substrates; blue curve, nucleated at 675 °C. The STEM images and 2D evaluation of the samples belonging to the green, red, and yellow curves are shown in Figure 1b and d, respectively, as well as Figure S6c–f.
observations of an interface with pyramidal features. This was achieved by modeling energetic and kinetic aspects independently: (i) ab initio computations of several possible interface orientations were performed to unveil energetic driving forces for the faceting and (ii) kinetic modeling of elementary growth processes was performed in order to comprehend the degree of intermixing observed. At first, the question arises whether computations can also lead to the intermixing of seven atomic layers as observed.

Growth processes are dominated by surface-diffusion of the atoms deposited. According to transition state theory, diffusion rates are determined by the activation energy required to move one atom to another minimum position on the surface. Thus, first-principles DFT computations were applied to determine the lateral diffusion barriers of Si, Ga, and P atoms on the surfaces apparent during growth. It turns out that for the Si(001)(2 × 1) surface used experimentally, the barriers for Si (0.34 eV) and Ga (0.11 eV) adatoms are much smaller compared to P (1.13 eV) adatoms. This is in line with previous experimental and theoretical studies: Diffusion barriers of 0.6–1.0 eV for Si adatoms, whereas lower barriers were calculated for Ga adatoms (<0.5 eV) and higher barriers for P adatoms (0.94 eV) compared to Si. A similar ratio of diffusion barriers for the adatoms Si, Ga, and P was found for the unreconstructed Ga- and P-terminated GaP(001) surfaces (Figure S7). In Figure 3, the hopping pathways for the adatoms for hopping across the dimer rows are considerably higher, which has been observed before.

The dynamic nature of the experimental deposition and interface formation can now be modeled by using these DFT results to make a rational choice of parameters for a large-scale KMC simulation of the growth procedure using a Bortz–Kalos–Lebowitz (BKL) algorithm. This method is applicable because elementary bonding processes and diffusion dominate the growth. We want to emphasize that we do not use a comprehensive list of DFT energy data to derive a first-principles KMC approach as has been done in the past. Instead, the empirical parameters describing the diffusion barriers in our KMC are chosen to represent the outcome of the DFT investigations, namely one species being less mobile than the others. Thus, although KMC is inherently a method not considering electronic structure, the information from ab initio computations is implicitly taken into account.

The simulation, run on a diamond cubic lattice, consisted of adsorption and diffusion events mimicking the epitaxial growth with a comparable growth rate of 1 monolayer/s (in flow rate modulated epitaxy growth mode) and a simulation temperature of 500 °C. Energy barriers for adatom hopping were calculated in an Arrhenius-type approach as a sum of bond energies to nearest and next-nearest neighbor atoms, which determine the mobility of the atomic species. The energy contribution of each pair of atoms was chosen as 0.3 eV for a nearest-neighbor and 0.15 eV for a next-nearest-neighbor bond, except for much stronger Si–P bonds (0.6 eV for nearest- and 0.2 eV for next-nearest-neighbor bonds, respectively), mimicking the significantly higher diffusion barriers of P atoms as obtained in the DFT calculations. (For a detailed discussion of the bond parameters see Supporting Information.) If the KMC is run with corresponding parameters, the experimentally observed amount of intermixed layers, as well as the structured morphology of the intermixed region is quantitatively reproduced. The depth indicates the same amount of intermixing, spanning approximately seven monolayers in the direction of growth (Figure 2a,b, red data points). Moreover, if one starts growth modeling on a smooth Si surface (Figure 4a), even the morphology of the GaP/Si interface region from KMC simulations is strikingly similar to the experimental observations of pyramid formation (Figure 4b, the GaP layer grown was removed to emphasize the Si interface structure). An exemplary slice through the model is shown in Figure 4c. Here, the viewing direction is [110] in analogy to the STEM investigations. The structured interface and the dimensions of the interface features observed in the experiment are reproduced very well in the KMC simulation. The simulated interface, as shown in Figure 4b, can be analyzed quantitatively by determining the elemental composition in each monolayer. The results can be compared to the experimental line scans across the interface, showing excellent agreement both for the thin and thick TEM samples (Figure 2a,b, red data points). The SD, as a measure for the degree of structuring of the intermixed region, also is well reproduced by the growth simulations, as evident from the lower part of Figure 2a,b. The increased discrepancy between simulation and experiment on the III–V side can be explained by noise in the experimental data, as discussed above. This agreement, notably, is found only if one diffusing species (here P) is less mobile than the others. If the same parameters are chosen for all species, the resulting interface structure is always interdiffused and not structured (Figure 2a, green data points). The width of the interdiffused

**Figure 3.** Minimum (Min) and transition state (TS) positions of Si, Ga, and P adatoms on a slab model of the Si(001) surface with (2 × 1) dimer reconstruction from atop. Adatom positions are indicated via arrow origin (Min) and arrowhead (TS). Barrier heights for diffusion along and across the dimer rows are given in electronvolts. For interrow hopping paths that exhibit a second minimum only the larger barrier is shown. Color code: Si, blue; P, green; Ga, orange.

On the Si(001)(2 × 1) surface are outlined. The pathways are thereby highlighted by red arrows with the origin being the starting position and the arrowhead marking the transition state of the hopping movement. One species (P atoms) thus is less mobile than the other species (Si and Ga atoms) in a microscopic analysis of diffusion on those surfaces. The barriers found for hopping along the dimer rows are in very good agreement with results derived for the simpler model of the unreconstructed surfaces (Figure S7), which is the same setup that is used in the KMC approach outlined below. The barriers
region then depends on the simulated growth temperature and is for a growth temperature of 500 °C much smaller than the experimentally observed intermixing. In short, the diffusion characteristics during growth mentioned above lead to an intermixing of atoms within an interface region of seven atomic layers.

However, the question remains, why do we find a structured, pyramidal interface morphology? Previous models suggested flat, one- or two-layer intermixed GaP/Si interfaces based on DFT computations and rationalized by electron-counting models.47,57 This puzzling finding can be understood from the relative stabilities of intrinsic interfaces, which we calculated by DFT, as KMC may not be able to describe the formation of distinct facets as especially electronic structure effects are neglected. Interface formation energies for GaP(001)/Si(001), GaP(111)/Si(111), and GaP(112)/Si(112) interfaces, also considering one transition layer, were determined (Figure 5).

In these computations, local stress and strain effects were considered by relaxation of all atomic positions and the c axis of the supercells. We found randomly intermixed structures over several layers to be much less stable. The interface formation energies \( \Delta E_{\text{if nonrelax}} \) are defined as

\[
\Delta E_{\text{if nonrelax}} = \frac{N}{2}(E_{\text{Si}} + E_{\text{GaP}}) - N \times E_{\text{GaP/Si}} / A_{(001)}
\]

(1)

where \( E_{\text{GaP/Si}} \) is the energy of the interface supercell, \( E_{\text{Si}} \) and \( E_{\text{GaP}} \) are the total energies of supercells of the same size containing only Si or GaP bulk material, respectively, and \( N \) is a normalization factor (1 for slab cells and 1/2 for bulk cells). \( \Delta E_{\text{if nonrelax}} \) is normalized to the unit cell area of the (001) interface \( A_{(001)} \), which is orthogonal to the material’s growth direction.58,59 The interface supercells subsequently were elongated along the c axis in steps of 0.05% of the lattice constant under epitaxy conditions (strain relaxation) and the atomic positions were relaxed within the supercell of optimal lattice constant c (lateral stress relaxation). The formation energies were then corrected by the relaxation contribution \( \Delta E_{\text{relax}} \) as
ΔE_if = ΔE_if^nonrelax − ΔE_if^relax

All ΔE_if values are positive, as expected for metastable materials that do not represent the global thermodynamic equilibrium structures.1 The configurations chosen for the DFT investigation of the GaP/Si interfaces represent flat, abrupt structures enclosing growth direction (001) and low-index interfaces (111) and (112). Additionally, we consider configurations (001)_d and (111)_d with one transition layer, where every second Si atom is substituted by Ga or P, following the early proposals by Harrison to achieve charge-compensated interfaces.17,61 The abrupt (112) interface is intrinsically charge-compensated due to the atomic configurations (details see below and Figure 6) and does not require a transition layer. Contrary to previous arguments predicting a diverging interface energy,1 a compensation of the interface dipole moment is not necessary and convergence is achieved with sufficiently large supercells. The supercells were constructed by elongating the silicon bulk cell by eight times the lattice constant in the respective direction and substituting half of the layers by GaP. This resulted in a (Si)_{16}(GaP)_{16} supercell for all interfaces with two atoms in each layer (see Figure 6). A vacuum region of 16.6 Å was added for the slab cells and the resulting surfaces were passivated by hydrogen atoms on both sides of the slab. The convergence of this approach was tested by additionally computing the interfaces with bulk models (Figure 6). The configurations with transition layers (001)_d and (111)_d were modeled with bulk supercells of the composition (Si)_{15}(transition layer)_{1}(GaP)_{15}(transition layer)_{1} and (Si)_{23}(transition layer)_{1}(GaP)_{23}(transition layer)_{1}, respectively. For all interfaces, two possible terminations were investigated. Because of a beneficial construction of supercells (Figure 6) and the normalization procedure used, the energies of different interfaces can be directly compared. Relaxation effects in the interface structures are considered in these energies but lead only to minor changes as was found before for coherent interfaces.57,59 This is in contrast to lattice-mismatched interfaces, where local strain effects were found to be more dominant.62 Also, considering configurational entropy only leads to minor corrections.

We find the Ga-terminated interface to be more stable compared to the P-terminated interface in all cases except (111) for (001) and (111) there are exclusive Si−Ga or Si−P contacts at the interface; for a definition of termination for

<table>
<thead>
<tr>
<th>Interface type</th>
<th>Structural model</th>
<th>Termination</th>
<th>Bonds at the interface</th>
<th>ΔE_if [e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) slab</td>
<td>Si−Ga (2x); Si−P (2x)</td>
<td>Ga+P</td>
<td>0.540</td>
<td></td>
</tr>
<tr>
<td>(001) bulk</td>
<td>Si−Ga (2x); Si−P (2x)</td>
<td>Ga+P</td>
<td>0.787</td>
<td></td>
</tr>
<tr>
<td>(111) slab</td>
<td>Si−Ga (2x); Si−P (2x)</td>
<td>Ga+P</td>
<td>0.393</td>
<td></td>
</tr>
<tr>
<td>(111) bulk</td>
<td>Si−Ga (2x); Si−P (2x)</td>
<td>Ga+P</td>
<td>0.250</td>
<td></td>
</tr>
<tr>
<td>(112) slab</td>
<td>Si−Ga (2x); Si−P (2x)</td>
<td>Ga+P</td>
<td>0.429</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6. Structural models (slab and bulk) and ΔE_if for the interfaces investigated by DFT. Si(−P/−Ga)_n (fifth column) indicates n P/Ga atoms binding to one Si atom at the interface for the given termination (fourth column). Color code: Si, blue; P, green; Ga, orange. For the representation in Figure 5b, data from slab cells was chosen for abrupt interfaces (001), (111) and (112) and data from bulk cells was chosen for the cells with transition layer (001)_d and (111)_d. [a] Abrupt interfaces can be represented in slab and bulk structural models. [b] Shown are the Ga-terminated interface models except for (111)_tl. P-terminated models are derived by exchanging P- and Ga-atoms. [c] According to eq 1 in eV A^-1-1001-cell. [d] Average of ΔE_if for both terminations in slab calculations. [e] The cell consists of two interfaces with identical terminations and configurations. Labels Ga- and P-termination are chosen according to the atom exhibiting two bonds to silicon. [f] The cells consist of two non-identical interfaces. Labels Ga- and P-termination are chosen according to the atom, which is part of the transition layer.
other interfaces, see Figure 6). For the (001) interface, which represents the growth direction, the structure with transition layer (001)$_t$ is more stable compared to the abrupt (001) interface, in accordance with previous findings. The (111) interface, which lies at 35° to the growth direction, exhibits similar stabilities to (001)$_t$. In this case, exchanging atoms leads to an energy increase for the (111)$_t$ configuration compared to (111). Regarding these orientations, the formation energies for both terminations are comparable, as was found previously for GaAs/ZnSe interfaces. By contrast, the Ga-dominated termination (112)$_{Ga}$ for the (112) interface is significantly more stable than the inverse P-dominated termination (112)$_P$. This results in (112)$_{Ga}$ being the most stable interface investigated. This can be understood by a close look at the chemical bonds at the interface between Si and nonsilicon atoms, which are often termed “wrong bonds” (Figure 6). They dominate the electrostatic stabilization of the respective interface. For (112)$_{Ga}$ one Si atom binds to two Ga atoms and two Si atoms have a bond to a P atom each. The inverse pattern is found for (112)$_P$ (one Si binding to two P and two Si binding to one Ga each). These distinct bonding patterns as the origin for the different stabilities of (112) interface terminations were postulated previously based on experimental and conceptual considerations, although with the inverse sign.

In a recent XPS study, the (001) interface was proposed to consist of Si–P bonds exclusively, although this is hard to rationalize based on charge neutrality arguments and the results shown here. The same pattern is also found for the (001)$_t$, (001)$_p$, and (111) interfaces: Si–Ga bonds destabilize less than Si–P bonds, and two bonds to nonsilicon atoms have a higher energy penalty than one bond (Figure 6). This might lead to the conclusion that simple bond counting is enough to estimate the interface stabilities. This is, however, not the case because no simple rule can be found to connect the stabilization energies of the interface configurations with Si binding to both Ga and P atoms (i.e., (001)$_p$ (111)$_t$ (112)) to the number of these bonds. Additionally, the ordering of the relative energies of the different interfaces cannot be explained by such a simple model. Only first principle calculations with good structural models are able to account for the chemical environment and deliver energies accurate enough for predictive analysis of these systems. The analysis of interface formation energies, thus, leads to the conclusion that (112)$_{Ga}$ interfaces should preferentially be formed.

How does this help us understand the formation of the seven-layer intermixed triangular structures observed experimentally? On the one hand, surface diffusion and KMC simulations lead to the conclusion that intermixing is a kinetically dominated growth effect and occurs if one species present is immobile. On the other hand, DFT-based interface stabilities reveal that there exists an energetic driving force to form other facets than the flat (001) orientation. Hence, pyramids containing (112) or (111) facets are likely to be formed in the experimental procedure. Energetically close-lying configurations (e.g., (112)$_{Ga}$ (111), and (001)$_P$) are likely to be formed as well, enabling the formation of the three-dimensional pyramidal shape observed in experiments. Nevertheless, these structures are overgrown during the continued deposition of GaP overlayers. Thus, the surface diffusion necessary to build the pyramids cannot continue and the resulting morphology is covered by bulk GaP. Pyramidal structures might form in the grown crystal, with one facet composed of the most stable Ga-terminated (112) interface and the other facets by the second or third most stable interfaces.

4. CONCLUSION

Quantitative atomic resolution STEM of GaP/Si reveals an intrinsic pyramidal interface morphology. This morphology is stable under a wide range of growth conditions and can only be altered if growth temperatures are set to unreasonable high values so that interdiffusion dominates. Theoretical modeling by KMC and DFT has shown that this faceted interface structure is indeed the stable one for the examined material system. These findings allow general conclusions to be made concerning interface formation in semiconductor growth processes via heteroepitaxy. If two materials with different polarity and element combinations with highly different electronegativities are grown, there is a strong influence of the chemical environment at the interface on its structural morphology (thermodynamic drive). In heteroepitaxy, not only strain plays a key role in the formation of interfaces. In addition, the different mobility of relevant species on the surface results in diffusion (kinetic drive) and determines the width of the interface region assembled.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b04896.

Supporting Information on the Si morphology prior to GaP growth by STM, the simulated HAADF STEM intensity, the atomically resolved structure of the interdiffused GaP/Si interface, all adatom hopping barriers from DFT and details of the Monte Carlo simulation is available. (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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