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Cite as: J. Vac. Sci. Technol. B **37**, 050602 (2019); https://doi.org/10.1116/1.5111715
Submitted: 29 May 2019 . Accepted: 19 July 2019 . Published Online: 12 August 2019

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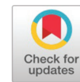

# Stability of epitaxial pseudocubic group IV-V semiconductors

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(Received 29 May 2019; accepted 19 July 2019; published 12 August 2019)

The semiconductor industry has developed complex growth methods to maximize the doping of contact regions and to minimize the contact resistance in semiconductor devices. These growth methods have created highly doped Si:P and Si:As films in which concentrations of the impurity as high as 10% are introduced with no visible precipitation. This work uses density functional theory to compare the relative stability of the dopant in a submicroscopic phase. Specifically, the stabilities of the pseudocubic $Si_3P_4$, $Si_3As_4$, $Ge_3P_4$, and $Ge_3As_4$ submicroscopic phases are analyzed at the level of density functional theory. The stability of these phases is analyzed as a function of strain in two dimensions, representing epitaxial growth, and three dimensions, representing inclusions in an extended matrix. The results show that both strained and unstrained extended pseudocubic $Si_3P_4$ and $Si_3As_4$ phases are thermodynamically unstable relative to SiP and $SiP_2$, and SiAs and $SiAs_2$, respectively. The extended forms of pseudocubic $Ge_3P_4$ and $Ge_3As_4$ phases are also thermodynamically unstable under epitaxial strain and volumetric strain. Because this work strongly suggests that extended phases $Si_3P_4$, $Si_3As_4$, $Ge_3P_4$, and $Ge_3As_4$ are not stable under experimental growth conditions, high levels of doping of Si or Ge by P or As most likely result in the formation of dispersed dopant clusters or a dispersed phase rather than the formation of submicroscopic pseudocubic phases of the dopants. *Published by the AVS.* https://doi.org/10.1116/1.5111715

## I. INTRODUCTION

The continuous decrease in contact area of semiconductor devices requires further increases in the doping of the semiconductors in order to mitigate the increase of contact resistance. New approaches are needed to provide high doping for lower contact resistance and high strain for improved carrier mobility.[1] Silicon doped with carbon and phosphorous (Si:CP) has been the material of choice, with the thin film providing tensile strain for electron mobility enhancement. However, because of the solubility limits in silicon, only a limited concentration of carbon and phosphorous dopants is possible using conventional epitaxial growth methods. At high dopant concentrations, C and P compete for substitution sites causing two problems: C is more likely to precipitate, and the P activation is limited by the C concentration. New methods of chemical vapor deposition (CVD) have enabled the growth of highly doped (HD) Si:P,[2,3] which provides a strain comparable to Si:CP. These methods may use low temperature, low pressure cyclic deposition etch processing, which commonly uses $Si_3H_8$, as the precursor or high temperature, high pressure coflow processing which utilizes dichlorosilane ($Si_2Cl_2H_2$).[3] By employing this complex growth scheme, it has been shown that phosphorus can be introduced at concentrations up to 10% with no visible signs of extended defects.[4–6] A record low contact resistance has been achieved with this material via the use of a postgrowth anneal.[4] While the origin of the strain and the positions of the phosphorus in the lattice have not been firmly established, the presence of a dispersed nonequilibrium Si:P phase was suggested in earlier works.[5]

Evidence for the presence of such pseudocubic $Si_3P_4$ phases has only appeared recently. Ye *et al.* analyzed CVD grown HD Si:P with Rocking Curve High Resolution X-ray Diffraction (RC HRXRD).[5,7,6] They concluded that the observed strain arose from phosphorus atoms clustered locally into pseudocubic $Si_3P_4$ complexes. Based on Hall effect and TEM data, Weinrich concluded that HD Si:P contained substitutional phosphorous, clusters of phosphorous vacancies, and clusters of phosphorus interstitial clusters.[8,9] Dhayalan *et al.* inferred the existence of an Si monovacancy surrounded by phosphorus from positron annihilation spectroscopy showing an excess of vacancies. However, they also concluded that the observed strain does not require the presence of $Si_3P_4$ complexes, but can be explained by phosphorous doping alone,[10,11] although others have found that the $Si_3P_4$ complexes are necessary to explain the strain.[9]

Density functional theory (DFT) studies of pseudocubic form of $Si_3P_4$ have shown it to have a negative enthalpy of formation.[12] Based on these calculations and the HRXRD results, these clusters have been proposed as the mechanism of accommodation of the excess phosphorus.[6] These DFT studies also examined $Si_3As_4$, $Ge_3As_4$, and $Ge_3P_4$ and also showed that they too have negative enthalpies of formation.[12] In a single unit cell of silicon, this phase can be viewed as a cluster of four phosphorus atoms around a vacancy or an $Si_3P_4$ defect. DFT calculations show that the $Si_3P_4$ defect is stable at high phosphorous concentrations.[13,14] Previous studies have not explored the possibility of $Si_3P_4$ growing epitaxially as a submicroscopic ordered phase; that is, a phase on the length scale below that resolvable by TEM. This letter, therefore, analyzes the thermodynamic stability of these defective zinc blende structures with respect to the known phases by constructing free-energy convex hulls[15–19] of the binary systems. In addition, the effect of epitaxial strain from the Si and Ge substrates and volumetric strain on the extended phases is also studied.

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 2166-2746/2019/37(5)/050602/4/$30.00 

## II. COMPUTATIONAL METHODS

The DFT calculations use the plane-wave method as implemented in Vienna *Ab initio* Simulation Package. The generalized gradient approximation is used for the exchange-correlation effects.[20–23] Pseudopotentials are described by the projector augmented wave (PAW) method.[20,22,23,21] A supercell of $2 \times 2 \times 2$ is used for convex hull calculations. A $3 \times 3 \times 3$ Monkhorst-Pack k-points mesh is used for the Brillouin zone sampling. The converged plane-wave cutoff energies are 310, 290, 300, and 350 eV for $Si_3P_4$, $Si_3As_4$, $Ge_3P_4$, and $Ge_3As_4$, respectively. For unconstrained bulk calculations, the cell parameters and atomic positions are relaxed simultaneously until the force on each atom is less than 0.01 eV/Å, and the components of stress are less than 0.02 GPa. To mimic the strain effect of epitaxial growth, A supercell for each phase was chosen such that the lattice would be commensurate with the substrate material. The supercell lattice in the a and b directions (i.e., normal to the growth direction) is set to those of Si or Ge. The cell parameters are relaxed in the direction normal to the epitaxial plane (c-direction) only, and the atomic positions are relaxed to the same force limit. In order to consider a precipitate, the supercell is again made commensurate with the substrate material, and the supercell lattice parameters in all three directions are fixed to those of the Si or Ge matrix in which it is embedded, and only atomic relaxations are allowed. In all calculations, the atom positions are optimized such that the force on every atom is small, and the interface between the substrate and phases is not included in the calculations. The d-orbital electrons are included in the Ge potential.[24]

## III. RESULTS AND DISCUSSION

As Fig. 1 shows, the $Si_3P_4$ structure is like the zinc blende structure but with the atom at the center of one face absent; we designate this plane as (100). This means that from a crystallographic point of view the structure is tetragonal. However, the three lattice constants for the $Si_3P_4$ phase are essentially the same ($a = b = 5.0929$ Å, $c = 5.0928$ Å); that is, the structure can be considered pseudocubic. The near equality of the lattice parameters arises from the atomic relaxation of the P atoms. These calculated lattice constants are consistent with the film strain determined from RC HRXRD.[3,5]

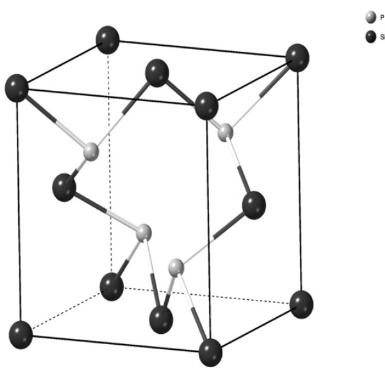

FIG. 1. Structure of pseudocubic $Si_3P_4$ is a defective zinc blende structure; note the absence of Si atoms (black) on the front and back faces of the cube. The P atoms (gray) are in the interior of the unit cell.

Other compositions are also present in the SiP binary system. In particular, the stable SiP and $SiP_2$ phases have been studied experimentally; microscopy has found them to be orthorhombic in silicon films.[25,26] From solid reaction and ion implantation studies, SiP and $SiP_2$ form as precipitates in Si films at high P concentrations. Though SiP and $SiP_2$ precipitate at high P concentrations, HD Si:P layers are grown far from equilibrium at low temperatures ($400 - 500\,°C$)[5,6] well below the much higher temperatures where the equilibrium SiP and $SiP_2$ phases are typically observed ($900 - 1400\,°C$).[15–17] These compositions do form the convex hull of this work, so they provide a reference for the stability of $Si_3P_4$. The pseudocubic $Si_3P_4$ structure has not been observed experimentally in TEM. However, its structure is similar to that of silicon, so it would not be expected to be visible using high resolution or high angular dark field STEM microscopy. The only indications for the existence of an $Si_3P_4$ material are the earlier DFT calculations.[5,27]

The energy of the Si:P system as a function of composition is shown in Fig. 2(a). The squares are the data for the stress-free system; the square line is the associated convex hull. This shows that the SiP and $SiP_2$ phases are stable. The $Si_3P_4$ pseudocubic structure lies 45 meV above the convex hull. Based on the analysis of a 29 902 inorganic materials. Sun *et al.* identified 70 meV as being an upper limit for metastability for most materials.[28] That is, if a structure lies more than 70 meV above the convex hull it is likely to decompose; if it lies less than 70 meV above the convex hull there is some chance that it will be metastable, most particularly if the metastable phase was actually the stable phase at some point in the processing history of the structure. Thus, though energetically disfavored to decomposition relative to the SiP and $SiP_2$ phases, $Si_3P_4$ might show metastability.

For epitaxy on an Si substrate (open square and line symbols), there is only a small increase in energy for the SiP and $SiP_2$ phases, but a larger increase in energy for $Si_3P_4$. It now lies 101 meV above the convex hull; based on the analysis of Sun *et al.*, it is likely to be unstable relative to SiP and $SiP_2$. The germanium substrate (open triangle) has a larger effect on the stability. In particular, while $SiP_2$ remains stable, SiP is only marginally stable, lying essentially on the line between Si and $SiP_2$. Epitaxy on Ge further increases $Si_3P_4$ above the convex hull (198 meV), increasing its driving force to decomposition. The corresponding precipitate cases show that SiP and $SiP_2$ are again stable for an Si matrix, while only SiP is stable for the germanium matrix. Thus, for all cases considered, the energy of $Si_3P_4$ is above the convex hull (169 meV for the Si matrix and 602 meV for the Ge matrix), and it can be expected to decompose under these conditions. We thus conclude that strain does not stabilize the $Si_3P_4$ pseudocubic phase.

Although they have not been explored experimentally, it is of interest to characterize the corresponding energetics for the Si:As, Ge:P, and Ge:As systems. Figure 2(b) illustrates the stability for the Si:As system. The convex hull for Si:As is similar to that

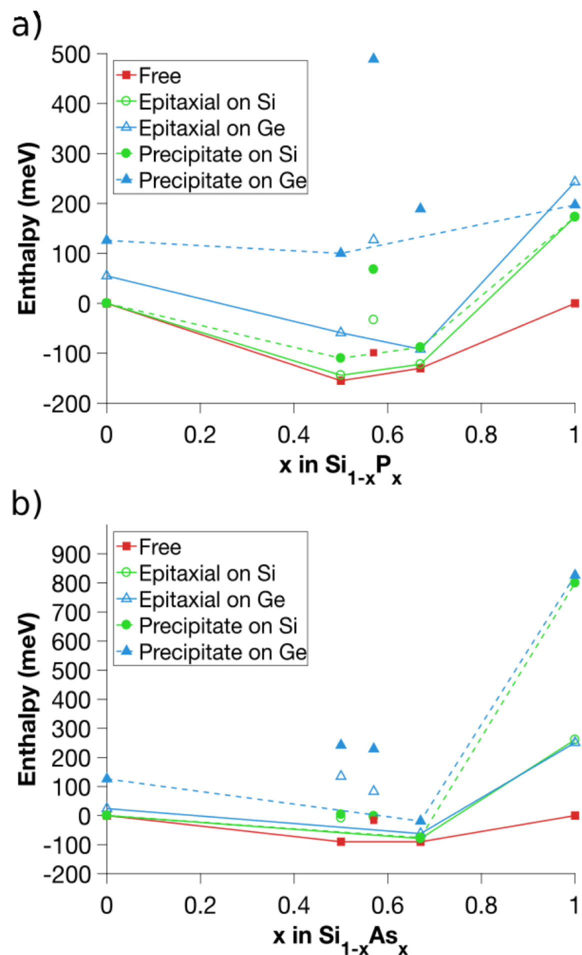


FIG. 2. Stabilty of SiB, $Si_3B_4$, and $SiB_2$ in the bulk (squares), on an Si substrate (circle), and on a Ge substrate (triangle) for (a) Si:P and (b) Si:As. For the epitaxial case, a hollow circle is used, and a filled circle for the precipitate case. Note that the energy scales are not all the same.

of Si:P for the bulk. For the unstrained system, as for the Si:P system, SiAs and $SiAs_2$ are stable, with $Si_3As_4$ lying 74 meV above the convex hull. For epitaxy on an Si substrate, only the $SiAs_2$ phase is stable. $SiAs_2$ remains stable as a precipitate in Si and is marginally stable as a precipitate in Ge. Interestingly, for both epitaxial strain and volumetric strain, $Si_3As_4$ is closer to the convex hull (62 and 66 meV, respectively). These are close to the limit of metastability, so it is possible, though unlikely, that they could be present. For epitaxial and volumetric strain in Ge, $Si_3As_4$ is 180 and 227 meV above the convex hull, respectively, and thus is predicted to be unstable.

Previous computational work on the GeP phase was not found, so the SiP structure was used as a prototype, and the lattice constants for GeP are comparable to the XRD data of Wadsten *et al.*[18] The $GeP_2$ phase was constructed based on the previous computational work, which found the tetragonal phase to be the most stable structure.[29] The bulk Ge:P system shows a stable GeP phase with a small formation energy and unstable $GeP_2$ and $Ge_3P_4$ phases. The $Ge_3P_4$ phase lies 48 meV above the convex hull and thus might be metastable. All of the strain conditions on an Si substrate stabilize the GeP phase relative to the stress-free condition. The epitaxial strain on Si increases the energy of $Ge_3P_4$ to 63 meV above the convex hull, while the volumetric strain increases it further to 97 meV. The epitaxial strain from a Ge substrate increases the metastability of $Ge_3P_4$ to 119 meV, but this is reduced to 66 meV under volumetric strain (Fig. 3).

Finally, in the absence of strain, GeAs and $GeAs_2$ are very weakly stable, $Ge_3As_4$ lies 48 meV above the convex hull. The energy of $GeAs_2$ is only weakly affected by the strain and remains stable for both epitaxial and precipitate conditions. For silicon epitaxy, GeAs lies just above the convex hull, while it is marginally stable as a precipitate in Si. Most interestingly, the effect of an Si substrate changes energies in such a way that $Ge_3As_4$ lies 20 meV above the convex hull for both epitaxial and volumetric strain conditions. It is thus possible that metastable $Ge_3As_4$ could be present.

Overall, $A_3B_4$ (A = Si, Ge; B = P, As) stoichiometries are not predicted to be thermodynamically stable either in bulk or under epitaxial or volumetric strain in either Ge or Si. However, the metastability, as measured by the distance above the convex hull, is small enough in some cases, such that their manifestation under some processing conditions cannot be ruled out.

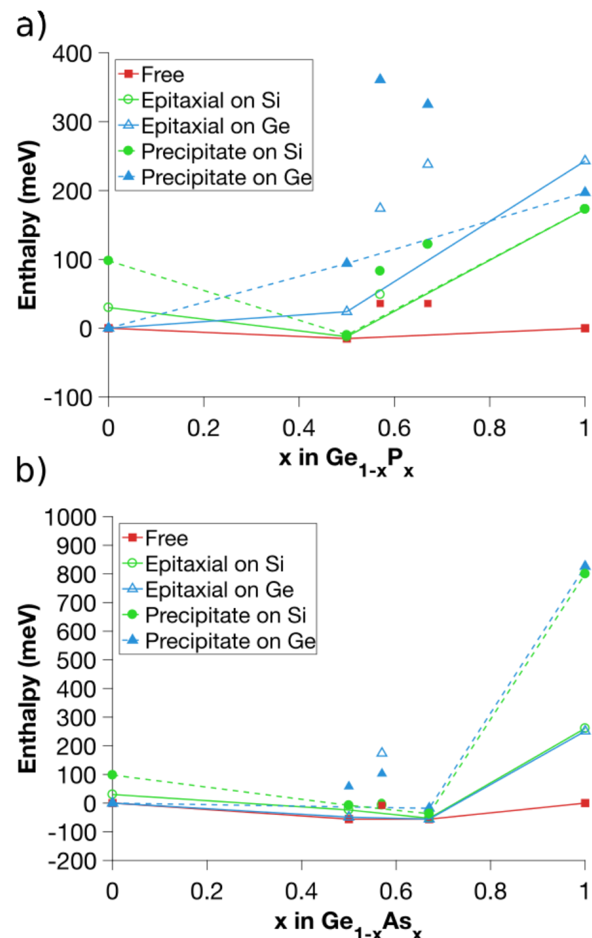


FIG. 3. Stabilty of GeB, $Ge_3B_4$ and $GeB_2$ in the bulk (squares), on an Si substrate (circles), and on a Ge substrate (triangles) for (a) Ge:P and (b) Ge:As. For the epitaxial case, a hollow circle is used, and a filled circle for the precipitate case. Note that the energy scales are not all the same.

There is considerable disagreement in the literature concerning the effect of laser annealing on the tensile strain. Some studies have shown an increase in the tensile strain;[6] others have shown a decrease.[9,11] Thus, it remains unclear under what laser annealing conditions the $Si_3P_4$ complexes break up and when or how they contribute to the active dopant concentration.

This work shows that an extended ordered phase of $Si_3P_4$ is not thermodynamically favored. The stability decreases with epitaxial and volumetric strain such that the ordered pseudocubic phase has a thermodynamic driving force for decomposition. No precipitates or extended defects are observed with microscopy techniques. Therefore, the experimentally observed strain does not appear to be associated with lattice mixing between submicroscopic $Si_3P_4$ and silicon, but rather the formation of a concentration of randomly dispersed $Si_3P_4$ complexes. This scenario is likely to play out in the Si:As, Ge:P and Ge:As systems also. Consistent with this conclusion, extended X-ray absorption fine structure experiments have concluded the existence of $As_4V$ defects in Si:As at temperatures below 750 °C.[30] Positron annihilation spectroscopy has also concluded the existence of vacancy centered arsenic defects postgrowth.[31]

HD Ge:As films have not yet been grown. However, Milazzo *et al.* ion implanted Ge wafers with arsenic above the solubility limit; these wafers were then laser annealed to achieve a similar highly doped Ge:As film on a Ge wafer.[32,33] Their RC HRXRD work found an epitaxial compressive strain layer. Based on our lattice calculations, a tensile strain is expected for a Ge substrate, and the pseudocubic $Ge_3As_4$ enthalpy of formation is above 0 eV for all cases. We therefore conclude that a defect complex other than $Ge_3As_4$ must be causing the compressive strain of the film.[32,33] The highly doped Ge:P film has not been grown on Si or Ge. However, this work does not predict a pseudocubic phase will form.

## IV. SUMMARY AND CONCLUSION

In conclusion, DFT calculations have shown that submicroscopic pseudocubic phases of Si:P, Si:As, Ge:P, and Ge:As are not thermodynamically stable as epitaxial films on or as precipitates in Si or Ge. It is possible, though unlikely, that the ordered pseudocubic phase of $Si_3P_4$ could be metastable under Si epitaxial conditions. It is also predicted that the submicroscopic pseudocubic $Ge_3As_4$ and $Ge_3P_4$ phases are not energetically favorable in the bulk unstrained case. If these films were experimentally grown under strained conditions, an ordered submicroscopic pseudocubic phase is also not predicted to form. For the first time, the GeP phase was found to be stable, and the lattice constants within agreement of XRD experiments. However, the $GeP_2$ tetragonal phase was not found to be stable in the bulk calculations, and the Ge:P system was not found to have any stable phases for epitaxial systems.

## ACKNOWLEDGMENTS

D.L.B. would like to thank the McKnight Doctoral Fellowship for funding this work. The authors also thank Michele Fullarton, Stephen Xie, Shubham Pandey, and Joshua Paul for useful discussions.

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