

Effective Doping in Cubic Si₃N₄ and Ge₃N₄: A First-Principles Study

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First-principles calculations have been conducted to investigate impurities in cubic Si₃N₄ and Ge₃N₄. Impurity species suitable for *n*- and *p*-type doping are suggested, in terms of the formation and ionization energies. The suggested species are P and O as *n*-type dopants and Al as a *p*-type dopant for c-Si₃N₄, and Sb and O as *n*-type dopants and Al as a *p*-type dopant for c-Ge₃N₄. The dependence of the formation energies on the chemical potentials indicates that a proper choice of growth conditions is mandatory for suppressing the incorporation of these impurities into anti and interstitial sites, where the impurities can be charged to compensate carriers.

I. Introduction

 $S^{\rm ILICON\ NITRIDE}\ (Si_3N_4)$ is an important material for structural applications, based on its outstanding high-temperature properties. Two known polymorphs, hexagonal α - and β -Si₃N₄, have been used as structural components. Recently, a third crystalline phase, in the cubic spinel structure (c-Si₃N₄), has been discovered through high-pressure and high-temperature experiments.¹ This novel phase has very low compressibility; the bulk modulus is reported to be ~ 300 GPa.¹⁻⁴ Concerning the electronic structure, No et al.⁴ has shown, through first-principles calculations within the local density approximation (LDA), that $c-Si_3N_4$ has a direct bandgap of 3.45 eV. This is in contrast to the bandgaps of α - and β -Si₃N₄, which are wider and indirect.^{5,6} Although the calculated bandgap may be somewhat underestimated, because of the LDA, $c-Si_3N_4$ is likely to fall into the category of wide-gap semiconductors. This classification implies potential applications of c-Si₃N₄ to optical and/or electrical devices that use its conductivity.

 Ge_3N_4 in the cubic spinel structure (*c*-Ge₃N₄) is also a novel high-pressure phase that has been subsequently synthesized to $c-Si_3N_4$.^{7,8} Similarly to $c-Si_3N_4$, this phase has been reported to exhibit lower compressibility than that of other phases.^{9,10} Dong et al.¹⁰ have shown, by LDA calculation, that the bandgap of this phase is 2.17 eV. Those researchers also performed a more elaborate calculation, based on the generalized density-functional theory, and obtained a direct bandgap of 4.0 eV.¹⁰ Apparently, c-Ge₃N₄ is also used as a semiconductor. Good dopants are essential for attaining semiconducting $c-Si_3N_4$ and $c-Ge_3N_4$. Previously, we have suggested impurity species appropriate to the doping of c-Si₃N₄, based on first-principles calculations.¹¹ In the

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present study, we conducted similar calculations to investigate impurities in c-Ge₃N₄, as well as in c-Si₃N₄. Impurity species suitable for n- and p-type doping, in terms of the formation and ionization energies, are proposed here.

II. **Computational Procedure**

The calculations were conducted by a first-principles planewave pseudopotential method, using the CASTEP program code (Accelrys, Inc., San Diego, CA),¹² within the generalized gradient approximation.¹³ Fifty-six-atom supercells, each containing an impurity, were used for c-Si₃N₄ and c-Ge₃N₄. For the impurity species, we considered B, Al, and Ga from Group III and P and As from Group V to substitute for Si in c-Si₃N₄. Carbon from Group IV and O and S from Group VI were adopted to substitute for N. Similarly, Al, Ga, In, P, As, Sb, O, S, C, and Si were considered for c-Ge₃N₄. The other elements in these groups were not investigated, because they are unlikely to dope effectively, as a result of significant size mismatch. For Si(Ge)-site substitution, the two types of Si(Ge) sites in the spinel structure, i.e., the tetrahedral and octahedral sites of the N-sublattice in the face-centered cubic structure, were considered. Hereafter, these sites are denoted t- and o-Si(Ge) sites.

For the supercell calculations, ultrasoft pseudopotentials¹⁴ with a plane-wave cutoff energy of 360 eV were used. This energy was confirmed to achieve convergence of the formation energies within 0.05 eV, relative to cutoff energies up to 700 eV for Ga and O impurities, which were expected to require relatively large cutoff energies because of localized 3d or 2p states. Numerical integration over the Brillouin zone was conducted at the Γ point. Because the valence- and conduction-band edges are located at the Γ point in c-Si₃N₄ and c-Ge₃N₄, the use of only the Γ point and a large supercell was considered a good strategy for simulating a dilute solution of impurities, as described elsewhere.¹⁵ The positions of the atoms within the second-nearest neighbors of the impurities were relaxed under a constant volume condition, until the residual forces for the relaxed atoms were <0.1 eV/Å. The lattice constants were determined through calculations for the primitive cells, using a plane-wave cutoff energy of 360 eV and 10 k points in the irreducible part of the Brillouin zone. The calculated values are 98.7%–98.9% of the experimental values reported for $c-Si_3N_4^{3,16-18}$ and 98.1% of those for $c-Ge_3N_4^{.8}$

The formation and ionization energies of the impurities were evaluated using the total energies of the supercells. The formation energy depends on the atomic chemical potentials and the Fermi energy $^{19-21}$ and, for c-Si₃N₄, is given as

$$E_{\text{formation}}(q) = E_{\text{T}}(q) - n_{\text{Si}}\mu_{\text{Si}} - n_{\text{N}}\mu_{\text{N}} - \mu_{\text{X}} + qE_{\text{F}}$$
(1)

where $E_{\rm T}$ is the total energy of a supercell containing an impurity atom in a charge state, q; $n_{\rm Si}$ and $n_{\rm N}$ represent the number of Si and N atoms, respectively, in the supercell; μ_{si} , μ_N , and μ_x are the chemical potentials of Si, N, and the impurity atoms, respectively; and $E_{\rm F}$ is the Fermi energy. For charged impurities $(q \neq 0)$, the total charge of the supercells was neutralized, using a jellium

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background. Energy shifts associated with jellium neutralization were estimated by the total energy difference between the neutral (normal) and the charged supercells of a perfect crystal; e.g., for positively charged perfect crystals, electrons were removed from the valence-band maximum, and jellium neutralization was included. Correcting this energy shift should correspond to setting the valence-band maximum to be the reference of the Fermi energy; thus, the total energies of the supercells with positively charged impurities, $E_{\rm T}(q)$ for q > 0, were evaluated with this reference. Negatively charged systems were dealt with in the same manner, except that the conduction-band minimum was used as the reference.

Assuming thermal equilibrium, the atomic chemical potentials associated with the host material, μ_{Si} and μ_N , are correlated as

$$3\mu_{\rm Si} + 4\mu_{\rm N} = \mu_{c-{\rm Si}_3{\rm N}_4({\rm bulk})} \tag{2}$$

where $\mu_{c-Si_3N_4(bulk)}$, the chemical potential of the bulk $c-Si_3N_4$, is a constant. This value was calculated as the total energy of $c-Si_3N_4$ per unit formula. The total energies per atom for bulk Si and $\alpha-N_2$ were chosen as the upper limits of μ_{Si} and μ_N , respectively. Thus, μ_{Si} and μ_N could vary within the following ranges:

$$\mu_{\mathrm{Si(bulk)}} + \frac{1}{3}\Delta H < \mu_{\mathrm{Si}} < \mu_{\mathrm{Si(bulk)}} \tag{3}$$

$$\mu_{\mathrm{N(bulk)}} + \frac{1}{4}\Delta H < \mu_{\mathrm{N}} < \mu_{\mathrm{N(bulk)}} \tag{4}$$

Here, ΔH is the calculated heat of formation of c-Si₃N₄ (-9.7 eV). In addition, the upper limit of μ_X is determined by the solubility limit, which corresponds to the condition that an impurity element just starts to segregate, in the form of either a simple substance or a compound. In other words, c-Si₃N₄ doped with an impurity is in equilibrium with the simple substance or the compound at the limit. Under equilibrium conditions, the chemical potentials of the impurities were determined using the total energies of the simple substances and of some compounds, which were calculated after optimization of the structure. The formation energies of the impurities in c-Ge₃N₄ were obtained in the same manner.

The ionization energies were evaluated as the difference between the formation energies of the neutral and the charged impurities, at a Fermi energy the same as the conduction-band minimum and the valence-band maximum for positive and negative ionization, respectively. These values are independent of the atomic chemical potentials. The energy of the conduction-band minimum was measured, from the valence-band maximum, as $\{E^{(1)} - E^{(0)}\} - \{E^{(0)} - E^{(-1)}\}\)$, where $E^{(N)}$ indicates the total energy of a perfect lattice supercell with additional N electrons. The resultant energies were 3.62 and 2.49 eV for $c-\text{Si}_3\text{N}_4$ and $c-\text{Ge}_3\text{N}_4$, respectively. These values show satisfactory agreement with bandgaps in the one-electron band structure of the primitive cells, 3.66 and 2.53 eV, respectively.

III. Results and Discussion

The calculated ionization energies of the impurities are listed in Table I. Those values correspond to single ionization; further ionization is unlikely for any of the impurities, because the calculated ionization energy was much higher.

For c-Si₃N₄, all of the candidates for n-type dopants exhibit ionization energies of <0.1 eV. Regarding Si-site substitution, the ionization energies depend strongly on the substitution sites. The P and As impurities at the o-Si sites are quite high in energy, indicating that only doping into the t-Si sites is effective. For p-type doping, the B and Al impurities show low ionization energies at both the t- and the o-Si sites. On the other hand, Ga and C impurities should be too high in ionization energy to work effectively as dopants. Thus, we regard P, As, O, and S impurities as good candidates for n-type dopants, and B and Al impurities as good candidates for p-type dopants, in terms of their ionization energies. Similarly, As, Sb, O, and S impurities and Al and Ga impurities should be favorable candidates as n- and p-type dopants,

Table I. Ionization Energies of Impurities in $c-Si_3N_4$ and $c-Ge_3N_4$

Impurity	Substitution	Ionization energy (eV)			
element	site	c-Si ₃ N ₄	c-Ge ₃ N ₄		
	<i>n</i> -Type D	Oopant			
Р	t-Si(Ge)	0.1	0.2		
	o-Si(Ge)	0.4	0.2		
As	t-Si(Ge)	0.0	0.1		
	o-Si(Ge)	0.8	0.4		
Sb	t-Si(Ge)		-0.1		
	o-Si(Ge)		-0.1		
0	N	0.1	0.1		
S	Ν	0.1	-0.1		
	<i>p</i> -Type	Dopant			
В	t-Si(Ge)	-0.1			
	o-Si(Ge)	0.0			
Al	t-Si(Ge)	0.0	-0.0		
	o-Si(Ge)	0.1	0.0		
Ga	t-Si(Ge)	0.2	0.1		
	o-Si(Ge)	0.5	0.4		
In	t-Si(Ge)		0.3		
	o-Si(Ge)		0.8		
С	Ň	0.7	0.5		
Si	Ν		1.7		

respectively, for c-Ge₃N₄. Hereafter, we focus on these impurities and assess them from the viewpoint of formation energies.

Figures 1 and 2 show the formation energies of the impurities in the neutral charge state. The energies were evaluated assuming the solubility limit, where the formation energies are given as a function of the Si(Ge) or N atomic chemical potential; the left and right sides of the figures correspond to the Si(Ge)-rich limit (e.g., $\mu_{Si} = \mu_{Si(bulk)}$ and $\mu_N = \mu_{N(bulk)} + \frac{1}{4}\Delta H$ for *c*-Si₃N₄) and the N-rich limit ($\mu_{Si} = \mu_{Si(bulk)} + \frac{1}{3}\Delta H$ and $\mu_N = \mu_{N(bulk)}$ for *c*-Si₃N₄), respectively. The change in slope indicates the transition of the reference materials, to determine the chemical potentials of the impurities at the solubility limit. As references, the following compounds were considered, in addition to the simple substances: SiP, SiP₂, SiAs, SiAs₂, SiO₂ (α -quartz), SiS₂, *c*-BN, and *w*-AlN for *c*-Si₃N₄; GeAs, GeAs₂, GeO₂, GeS, GeS₂, *w*-AlN, and *w*-GaN for *c*-Ge₃N₄.

For Si(Ge)-site substitution, N-rich conditions are preferable in formation energy, whereas Si(Ge)-rich conditions are preferable for N-site substitution, as recognized in Figs. 1 and 2. The dependence of the formation energies on the chemical potentials is much stronger in c-Si₃N₄, because of the larger heat of formation; as shown in Eqs. (3) and (4), the chemical potentials can vary within the ranges given by the heat of formation, -9.7 and -3.6 eV for c-Si₃N₄ and c-Ge₃N₄, respectively.

Regarding the *n*-type doping of $c-Si_3N_4$, considered in Fig. 1(a), the P impurities to substitute for Si can be lowered in formation energy much more than the As impurities, under N-rich conditions. This difference suggests that the P impurities are more favorable as dopants, although their ionization energy is 0.1 eV higher than that of the As impurities, as shown in Table I. For N-site substitution, the S impurities are much higher in formation energy than the O impurities, indicating that the O impurities are preferable.

For the *p*-type dopants, shown in Fig. 1(b), the Al impurities clearly are preferable to the B impurities, in terms of the formation energies. The ionization energies shown in Table I imply that the Al impurities can work as acceptors at both the *t*- and the *o*-Si sites. These sites are likely to be occupied with nearly the same concentration, in view of the comparable formation energies.

In regard to the *n*-type doping of c-Ge₃N₄, the two candidates for Ge-site substitution, the As and Sb impurities, are similar in formation energy, as shown in Fig. 2(a). In this case, the Sb impurities, with lower ionization energies, are preferable. For N-site substitution, the O impurities are better than the S impurities, in terms of the formation energies, similarly to the case for c-Si₃N₄.



Fig. 1. Formation energies of impurities as (a) n- and (b) p-type dopants for c-Si₃N₄. Energies were evaluated for the neutral charge state, at the solubility limit; subscripts indicate the sites of the impurities.

For the *p*-type dopants, shown in Fig. 2(b), the Al and Ga are comparable in formation energy. In view of the ionization energies, the Al impurities are more favorable. The behavior of the Al impurities is similar to that in c-Si₃N₄; they exhibit nearly the same formation and ionization energies at both Si(Ge) sites.

Summarizing, we suggest P and O impurities as *n*-type dopants and Al impurities as *p*-type dopants for c-Si₃N₄. Similarly, Sb and O impurities and Al impurities are proposed as *n*- and *p*-type dopants, respectively, for *c*-Ge₃N₄.

We now consider the incorporation of these impurities into other sites. Previously, we investigated such effects for P, O, and Al impurities in $c-Si_3N_4$.¹¹ These impurities were likely to compensate carrier electrons or holes at anti and interstitial sites. However, incorporation of the impurities into these sites could be suppressed effectively when the formation energies for the normal substitutional sites were lowered; i.e., under N-rich conditions for the P and Al impurities and Si-rich conditions for the O impurities, as recognized in Fig. 1.

In the present study, the impurities at anti and interstitial sites were also investigated for c-Ge₃N₄. The results are summarized in Table II. The Fermi energy is taken to be the conduction-band minimum for Sb and O as *n*-type dopants and the valence-band maximum for Al as a *p*-type dopant. The formation energy corresponds to the charge state that gives the lowest energy under these conditions of Fermi energy.



Fig. 2. Formation energies of impurities as (a) n- and (b) p-type dopants for c-Ge₃N₄. Energies were evaluated for the neutral charge state, at the solubility limit; subscripts indicate the sites of the impurities.

For Sb and O impurities, the negative charge states at the anti or interstitial sites indicate that the impurities should trap carrier electrons when they occupy these sites. Similarly, Al impurities can be positively charged to compensate doped holes at the anti and interstitial sites. Therefore, incorporation of the impurities into these sites can be a serious problem during doping. However, occupation of anti and interstitial sites should be negligible for the Sb and O impurities, because the formation energies for these sites are quite high under any conditions of Ge or N chemical potential. On the other hand, the anti and interstitial sites are comparable in formation energy to the normal substitutional sites for Al impurities under Ge-rich conditions, indicating that N-rich conditions should be chosen. Thus, the growth conditions are a very important factor in doping, as well as the dopant species.

IV. Summary

The formation and ionization energies of impurities in c-Si₃N₄ and c-Ge₃N₄ have been investigated through first-principles calculations. Impurity species suitable for *n*- and *p*-type doping are suggested, in terms of these energies. The suggested species are P and O as *n*-type dopants and Al as a *p*-type dopant, for c-Si₃N₄,

Table II. Formation Energies of Impurities at Various Sites in a	-Ge ₃ f	N ₂
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Impurity site	Sb			0		Al			
	CS	Ge-rich	N-rich	CS	Ge-rich	N-rich	CS	Ge-rich	N-rich
t-Ge	1 +	3.3	2.1	6-	7.2	5.4	0	2.0	1.7
o-Ge	1 +	2.9	1.7	6-	7.9	6.1	0	1.8	1.5
N	2 -	9.5	10.4	0	1.0	1.3	6+	1.9	3.7
<i>t</i> -interstitial <i>o</i> -interstitial	$\frac{1+}{3+}$	13.7 15.0	13.7 15.0	$\frac{1-}{2-}$	7.7 5.5	7.1 4.9	3+3+	1.7 2.0	2.6 2.9

[†]Fermi energy is taken to be the conduction-band minimum for Sb and O as *n*-type dopants and the valence-band maximum for Al as a *p*-type dopant. Formation energy corresponds to the charge state (CS) that gives the lowest energy under these conditions of Fermi energy. Normal substitutional sites for Sb and Al are the *t*- and *o*-Ge sites, whereas that for O is the N site.

and Sb and O as *n*-type dopants and Al as a *p*-type dopant, for c-Ge₃N₄. Compensation of carriers as a result of the incorporation of these impurities into anti and interstitial sites can be suppressed by a proper choice of growth conditions. Although other factors, such as electron/hole mobility and self-compensation effects by native defects, contribute to electrical properties, the present information on dopants should be useful for attaining semiconducting c-Si₃N₄ and c-Ge₃N₄.

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