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Calculations of acceptor ionization energies in GaN

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The $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian and a model potential are used to deduce the acceptor ionization energies in GaN from a systematic study of the chemical trend in GaAs, GaP, and InP. The acceptors studied include Be, Mg, Ca, Zn, and Cd on the cation sites and C, Si, and Ge on the anion sites. Our calculated acceptor ionization energies are estimated to be accurate to better than 10% across the board. The ionization energies of C and Be (152 and 187 meV, respectively) in wurtzite GaN are found to be lower than that of Mg (224 meV). The C was found to behave like the hydrogenic acceptor in all systems and it has the smallest ionization energy among all the acceptors studied.

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I. INTRODUCTION

Despite the rapid progress in the development of the GaN-based devices, the *p*-doping is still an important issue.[1–4] The inefficiency in the *p*-doping is mainly due to the high ionization energies of the acceptors. For example, the most commonly used acceptors, Mg and Zn, have the ionization energies around 230 and 350 meV, respectively.[1–9] Thus the first step toward more efficient *p*-doping in GaN is to identify acceptors with smaller ionization energies than that of Mg. Unfortunately, the experimental identification of the acceptors and their ionization energies still have large uncertainties, which could arise from complications due to free-carrier screening, compensation of acceptors and donors, and different activation energies probed by different techniques.

The available theoretical calculations[10–14] have not narrowed these uncertainties. The basic problem is that there is no *ab initio* theory that allows an accurate calculation of the acceptor levels. However, recent calculations based on the spherical model[10,11] and the $\mathbf{k}\cdot\mathbf{p}$ theory[12–14] have provided a framework to study the acceptor levels.

In this work, we focus on the shallow (hydrogenic) substitutional acceptor states, because these are the most relevant states concerning the p-doping of semiconductors. In our approach, the $\mathbf{k}\cdot\mathbf{p}$ theory and a model potential are used to extend the chemical trend of the acceptor ionization energies from the more established GaAs, GaP, and InP systems to GaN. The acceptors studied include Be, Mg, Ca, Zn, and Cd on the cation sites and C, Si, and Ge on the anion sites. Based on our calculation, the ordering of the ionization energies for these impurities, namely Be$<$Mg$<$Ca$<$Zn$<$Cd and C$<$Si$<$Ge, is the same in all the four semiconductors studied. In terms of relevancy to application, we found that there are only two acceptors (C and Be) with smaller ionization energies (152 and 188 meV, respectively) than the value for the Mg (224 meV) acceptor currently used for the *p*-doping of wurtzite GaN. Our results should encourage a continuing investigation of C and Be for more efficient *p*-doping of GaN.

The rest of the paper is arranged as following. In Sec. II we describe the $\mathbf{k}\cdot\mathbf{p}$ theory and the model potential used in our calculation. In Sec. III, we develop a procedure to extend the chemical trend from the GaAs, GaP and InP to GaN and present the calculated acceptor ionization energies. Section VI summarizes the comparison with experiments and other theories and discusses the possibility to improve the *p*-doping efficiency in GaN. Section V concludes the present study.

II. METHOD

A. Acceptor states based on k·p Hamiltonian

Using the effective-mass approximation (EMA) for the shallow acceptor and the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian for the degenerate valence bands, the acceptor states are described by the following matrix equation:

$$[H(\mathbf{r})+U(\mathbf{r})\mathbf{I}]\mathbf{F}(\mathbf{r})=E\mathbf{F}(\mathbf{r}). \tag{1}$$

Here $H(\mathbf{r})$ is a r-space representation of the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian, $\mathbf{I}$ is the 6×6 unit matrix, and $\mathbf{F}(\mathbf{r})$ is a column vector whose column elements are the envelope functions $F_j(\mathbf{r})$.

The linear variational method is used to solve Eq. (1). The envelope functions $F_j(\mathbf{r})(j=1,\ldots,6)$ are expanded as a linear combination of the spherical harmonics with the hydrogeniclike redial functions:

$$F_j(\mathbf{r})=\sum_{l,m} f_l^j(r)Y_{lm}(\theta,\phi), \tag{2}$$

with

$$f_l^j(r)=\sum_{i=1}^{N} C_i^{jl} r^l \exp(-\alpha_i r), \tag{3}$$

where j is the hole band index, l is the angular momentum quantum number, and α_i are the exponents used. We found that about 10 α_i's centered about the inverse Bohr radii of acceptor are sufficient to obtain the converged ground state energies.

The $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian for the wurtzite semiconductors is the RSP Hamiltonian proposed by Bir and Pikus.[13] Although this $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian has appeared numerous times in the literature, we show its explicit form so our results can be reproduced

$$H_{wz}=\begin{Bmatrix} F & 0 & -H^* & 0 & K^* & 0 \\ 0 & G & \Delta & -H^* & 0 & K^* \\ -H & \Delta & \lambda & 0 & I^* & 0 \\ 0 & -H & 0 & \lambda & \Delta & I^* \\ K & 0 & I & \Delta & G & 0 \\ 0 & K & 0 & I & 0 & F \end{Bmatrix}, \tag{4}$$

where

$$F=(A_2+A_4)k^2+(A_1-A_2+A_3-A_4)k_z^2+\Delta_1+\Delta_2,$$

$$G=(A_2+A_4)k^2+(A_1-A_2+A_3-A_4)k_z^2+\Delta_1-\Delta_2,$$

$$H=-A_6k_yk_z+iA_6k_zk_x+iA_7(k_x+ik_y),$$

$$I=-A_6k_yk_z+iA_6k_zk_x-iA_7(k_x+ik_y),$$

$$K=A_5(k_x^2-k_y^2)+2iA_5k_xk_y, \tag{5}$$

$$\lambda=A_2k^2+(A_1-A_2)k_z^2,$$

$$\theta=A_4k^2+(A_3-A_4)k_z^2,$$

$$\Delta=\sqrt{2}\Delta_3,$$

$$k^2=k_x^2+k_y^2+k_z^2.$$

In the above, Δ_1 is the crystal-field splitting, Δ_2 and Δ_3 are the spin-orbital coupling constants, which are taken to be the same in our calculation. The A_i's for i from 1 to 7 are the parameters related to the inverse hole masses and the detailed band structures near the top of the valence band.

The corresponding Hamiltonian for zinc-blende (zb) semiconductors is the well-known Kohn-Luttinger (KL) Hamiltonian,[14]

$$H_{zb}=\begin{Bmatrix} P & L & M & 0 & N & Q \\ L^* & R & 0 & M & S & \sqrt{3}N \\ M^* & 0 & R & -L & \sqrt{3}N^* & S \\ 0 & M^* & -L^* & P & -Q^* & N^* \\ N^* & S^* & \sqrt{3}N & -Q & T & 0 \\ Q^* & \sqrt{3}N^* & S^* & N & 0 & T \end{Bmatrix}, \tag{6}$$

where

$$P=\frac{1}{3}(A+2B)k^2-\frac{1}{6}(A-B)(2k_z^2-k_x^2-k_y^2),$$

$$L=-\frac{C}{\sqrt{3}}k_yk_z-\frac{iC}{\sqrt{3}}k_zk_x,$$

$$M=\frac{1}{\sqrt{12}}(A-B)(k_x^2-k_y^2)-\frac{iC}{\sqrt{3}}k_xk_y,$$

$$R=\frac{1}{3}(A+2B)k^2+\frac{1}{6}(A-B)(2k_z^2-k_x^2-k_y^2),$$

$$S=\frac{i}{3\sqrt{2}}(A-B)(2k_z^2-k_x^2-k_y^2), \tag{7}$$

$$T=\frac{1}{3}(A+2B)k^2-\Delta_0,$$

$$N=iL/\sqrt{2},$$

$$Q=-i\sqrt{2}M,$$

$$k^2=k_x^2+k_y^2+k_z^2,$$

where Δ_0 is the spin-orbital splitting at $\mathbf{k}=0$. A, B, and C are related to the Luttinger parameters (γ_1, γ_2, γ_3), i.e., the inverse hole masses. By the use of the usual transformation $k_\beta\rightarrow -i(\partial/\partial x_\beta)$, the operator $H(\mathbf{k})$ is transformed to $H(\mathbf{r})$ used in Eq. (1).

The parameters in the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonians are given in Tables I and II. The valence band parameters of GaAs are from Binggeli and Baldereschi,[15] those for GaP and InP are

TABLE I. The valence band parameters, dielectric constant κ, and the bond lengths d of GaAs, GaP, InP, and zinc-blende (zb) GaN. Here d is in units of Å, the splitting Δ_0 is in units of meV, and the inverse hole mass parameters A, B, and C are in units of $\hbar^2/2m_0$.

Host	A	B	C	Δ_0	κ	d
GaAs [a]	15.18	3.06	17.46	340	12.56	2.45
GaP [b]	8.12	2.24	9.96	80	11.02	2.36
InP [b]	14.60	2.12	16.56	130	12.60	2.54
GaN [c]	5.06	1.16	5.85	19	9.50	1.95
GaN [d]	7.78	0.30	5.65	20	9.50	1.95
GaN [e]	7.18	0.54	6.13	11	9.50	1.95

[a] Reference 15.
[b] Reference 16.
[c] Reference 17.
[d] Reference 18.
[e] Reference 19.

TABLE II. The valence band parameters of wurtzite (wz) GaN. Here the splitting Δ_1 and Δ_2 are in units of meV, and the inverse hole mass parameters A_i ($i=1,\ldots,6$) are in units of $\hbar^2/2m_0$. The dielectric constant $\kappa=9.80$ is assumed for wurtzite GaN (Refs. 17–19).

Host	A_1	A_2	A_3	A_4	A_5	A_6	Δ_1	Δ_2
GaN [a]	6.36	0.51	−5.85	2.92	2.60	3.21	42.0	6.30
GaN [b]	6.56	0.91	−5.65	2.83	3.13	4.86	73.0	5.40
GaN [c]	7.24	0.51	−6.73	3.36	3.35	4.72	22.0	3.67

[a] Reference 17.
[b] Reference 18.
[c] Reference 19.

from Lawaetz *et al.*,[16] and the parameters of GaN are from Kim *et al.*,[17] Suzuki *et al.*,[18] and Yeo *et al.*[19] for both wurtzite and zinc-blende structures. The $\mathbf{k}\cdot\mathbf{p}$ parameters listed in Tables I and II for the wurtzite GaN correspond to the so-called quasicubic approximation, in which the linear terms in Eq. (5) are neglected by setting $A_7=0$. Although A_7 is important in describing the detailed valence bands for the wurtzite structures in general,[17] its values are very small for GaN and its inclusion is found to have little effect (less than 1 meV) on the acceptor ionization energies. Furthermore, in this approximation, the parameters A, B, and C of zinc-blende GaN, which are not presented in Refs. 18 and 19, can be obtained[17] from the available hexagonal parameters A_i $(i=1,\dots,6)$.

B. Model impurity potential

Since we want to use the experimental acceptor ionization energies of the more established semiconductors GaAs, GaP, and InP to deduce the chemical trend of the acceptor levels in GaN, we adopted a simple model potential that facilitates an accurate and efficient calculation. The potential contains all the necessary ingredients for an acceptor impurity potential. It has a form similar to the model potential used in our study of the donor states in SiC (Ref. 20) and GaN.[21] The model impurity potential $U(r)$ contains two terms

$$U(\mathbf{r})=U_0(\mathbf{r})+U_s(\mathbf{r}). \tag{8}$$

$U_0(\mathbf{r})$ characterizes the ionicity difference between the impurity and the host atom, and is represented by a spherical square-well potential of the radius r_a and the depth V_0, i.e.,

$$U_0(r)=\begin{cases}-V_0 & \text{for } r<r_a,\\ 0 & \text{for } r>r_a.\end{cases} \tag{9}$$

$U_s(\mathbf{r})$ is a screened Coulomb potential with a r-dependent screening function

$$U_s(r)=\begin{cases}(-e^2/\kappa r)[1+(\kappa-1)e^{-r/r_1}] & \text{for } r>r_b,\\ 0 & \text{for } r<r_b.\end{cases} \tag{10}$$

Note that $U_s(r)$ behaves as $-e^2/r$ for small r and as $-e^2/(\kappa r)$ for large r. Here κ is the dielectric constant of the host crystal.[15–17] The r_1 is a screening length which is taken as a constant for a given host. For different hosts, we treated r_1 as scaled proportional to the bond length of the host crystal. It turned out we could obtain very similar sets of final results with r_1 in GaAs varying from 0.7 to 0.85 Å. Here we simply choose $r_1=0.85$ Å. To leave as few adjustable parameters as possible, we take r_a to be the Pauling's covalent radius[22,23] of the impurity atom and r_b to be one half of the host bond length.[23] Furthermore, we assume that the difference in the V_0 is fixed between any two impurities substituting the same host atom. These conditions impose some constraints on the model potential. If it works well for the known cases, it may have a chance to do the same for GaN.

TABLE III. Calculated hydrogenic ionization energies E_A (in units of meV) for acceptor impurity in GaAs, GaP, InP, and GaN.

	GaAs	GaP	InP	GaN(wz)	GaN(zb)
E_A	25.5	53.5	38.9	150.4	137.2

III. CALCULATION PROCEDURE AND RESULTS

To give a reference, we first consider the simple hydrogenic model in which the impurity potential is taken to be $U(r)=-e^2/\kappa r$. The trial wave functions for the ground state only include the angular momentum components with $l=0$ and 2. The calculated acceptor ionization energies for GaAs, GaP, InP, and for both zinc-blende and wurtzite GaN using Kim *et al.*'s[17] $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian parameters are listed in Table III. These values are generally smaller than the experimental results. The difference measures the effect of the central-cell potential correction.

We note that the valence hole mass parameters in the literature have considerable variations. However, since the high energy spectra of an acceptor are mainly governed by the hole effective masses, one can use these spectra to refine the valence effective masses. The hole mass parameters of GaAs listed in Table I were deduced in this manner.[15] Therefore the resulting $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian for GaAs is used in our study without any further modifications. For the other systems, the valence band masses were either deduced from transport properties[16] or calculated directly from band structures.[17–19] For our calculation of the acceptor levels we will modify the inverse hole mass parameters by multiplying them by a factor η around 1. Note that $\eta=1$ for GaAs. The determination of η will be discussed later.

Since we have already fixed the other parameters in the potential, there are only are two adjustable parameters, V_0 and η, remaining. With a value of $r_1=0.85$ Å and $\eta=1$ already chosen for GaAs, the V_0 values are completely determined by the experimental acceptor ionization energies. The values of V_0 in Table IV for all the impurities, namely Be, Mg, Zn, and Cd on Ga sites and C, Si, and Ge on the As

TABLE IV. Calculated acceptor ionization energies E_A in GaAs. Here η is the inverse hole mass factor as defined in the context. The energies E and the potential depth V_0 are in units of meV, and r_a, r_b, and r_1 are in units of Å. The experimental data E_{expt} are taken from Ref. 24.

Impurity	E_A	E_{expt}	r_a	r_b	r_1	V_0	η
Be	28.1	28.0	1.06	1.22	0.85	1000	1.00
Mg	28.8	28.7	1.40	1.22	0.85	1300	1.00
Ca	30.4		1.74	1.22	0.85	1450	1.00
Zn	30.7	30.7	1.31	1.22	0.85	3400	1.00
Cd	34.6	34.7	1.48	1.22	0.85	4050	1.00
C	27.4	26.9	0.77	1.22	0.85	−2350	1.00
Si	35.2	35.2	1.17	1.22	0.85	7750	1.00
Ge	40.4	40.4	1.22	1.22	0.85	8650	1.00

TABLE V. Calculated acceptor ionization energies E_A in GaP. Here η is the inverse hole mass factor as defined in the context. The energies E and the potential depth V_0 are in units of meV, and r_a, r_b, and r_1 are in units of Å. The experimental data E_{expt} are taken from Ref. 24.

Impurity	E_A	E_{expt}	r_a	r_b	r_1	V_0	η
Be	56.7	56.6	1.06	1.18	0.82	1000	1.12
Mg	60.2	59.9	1.40	1.18	0.82	1300	1.12
Ca	67.4		1.74	1.18	0.82	1450	1.12
Zn	70.4	69.7	1.31	1.18	0.82	3400	1.12
Cd	95.0	102.2	1.48	1.18	0.82	4050	1.12
C	54.9	54.3	0.77	1.18	0.82	0	1.12
Si	169.3	210.0	1.17	1.18	0.82	10 100	1.12
Ge	281.7	265.0	1.22	1.18	0.82	11 000	1.12

TABLE VI. Calculated acceptor ionization energies E_A in InP. Here η is the inverse hole mass factor as defined in the context. The energies E and the potential depth V_0 are in units of meV, and r_a, r_b, and r_1 are in units of Å. The experimental data E_{expt} are taken from Ref. 24.

Impurity	E_A	E_{expt}	r_a	r_b	r_1	V_0	η
Be	40.4		1.06	1.27	0.88	100	1.14
Mg	41.2	40.0	1.40	1.27	0.88	400	1.14
Ca	43.0	43.0	1.74	1.27	0.88	550	1.14
Zn	47.2	47.0	1.31	1.27	0.88	2500	1.14
Cd	57.8	56.0	1.48	1.27	0.88	3150	1.14
C	40.3	41.4	0.77	1.27	0.88	0	1.14
Si	123.0		1.17	1.27	0.88	10 100	1.14
Ge	205.3	210.0	1.22	1.27	0.88	11 000	1.14

sites in GaAs, are obtained in this manner. Because the experimental acceptor ionization energy of calcium (Ca) in GaAs is not available, the V_0 value for Ca listed in Table IV was deduced from InP (see Table VI). We note that the V_0 values listed do not produce the exactly the experimental ionization energies, because we left some room to accommodate the experimental uncertainties and to improve the overall fitting for the other systems.

Next is to test the procedure in GaP. The V_0 values for the impurities on the Ga sites are taken to be the same as those in GaAs, because they are associated with the same set of impurities replacing the same host (Ga) atom. A direct calculation using the mass parameters in Table I in the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian yielded the correct chemical trend for the ionization energies for these acceptors. However, to improve the agreement between the calculated values with experiments, we adjust the scaling factor η for the inverse hole mass parameters. A value of $\eta = 1.12$ was found to produce an overall good result.

For the P-site impurities (C, Si, and Ge), since the mass parameters are already determined and the relative values of V_0 (the differences) are also fixed, we can only slide V_0 rigidly to obtain the best fit for the ionization energies. Our result shows that the C and Ge levels are good to within 10%, but the calculated Si level is about 40 meV lower than the experimental value quoted.[24] However, this experimental datum was adjusted by lowering a value of 77.9 meV from an earlier result.[24] Our calculated level is in middle of these two data. We feel that a further study of the Si acceptor level in GaP is needed.

For InP, the V_0 values for the impurities on the P sites are already determined from GaP. An adjustment of the inverse hole mass factor was able to obtain reasonable ionization energies for the two acceptors C and Ge with known experimental data. For the In-site impurities, a rigid shift of the V_0 values produced excellent ionization energies for all the impurities studied, as shown in Table VI.

The results of the acceptor levels in GaAs, GaP, and InP (see Tables IV, V, and VI) show that our potential model and the deduction procedure serve to bring together the experimental data. Our procedure not only correctly describes the chemical trend but also yields accurate ionization energies. We expect our method to work as well for GaN.

For GaN, we used three sets of the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonians[17–19] to test the internal consistency of our procedure. We started with the Kim *et al.*'s Hamiltonian.[17] Since the V_0 values for the impurities on the Ga sites are already determined from GaAs, we only need find the proper value for the inverse hole mass factor η. Because Mg is the most studied case, we adopted the experimental value of 224 meV in wurtzite (wz) GaN (Ref. 7) as the standard, which gives us a value of $\eta = 1.07$. It turned out that the same value of η also works well for the zinc-blende (zb) structure. The calculated level of 220 meV for Mg in zb-GaN falls in the middle of the experimental values of 213 (Ref. 25) and 230 (Ref. 26) meV. The other E_A values for the zb-GaN are just slightly smaller than that those in wz-GaN. With the value of η determined, we then rigidly shift the V_0 values for the N-site impurities to fit the only experimental value (224 meV) for Si in wurtzite GaN.[27] The parameters and the calculated acceptor levels for both wurtzite and zinc-blende GaN structures are listed in Table VII.

We then applied the same procedure to GaN with the other two sets of parameters[18,19] in the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian to test the internal consistency of the procedure. Since all the potential parameters for GaN are already determined in our model, we are only allowed to adjust the inverse hole mass factor η for these two sets of $\mathbf{k}\cdot\mathbf{p}$ Hamiltonians. This adjustment was done to bring the ionization energies of Mg to the same values (224 and 220 meV for the wurtzite and zinc-blende structures, respectively) as those in Table VII. We found that for these two sets of parameters, the inverse hole mass factor η for the zinc-blende structure is different from that for the wurtzite. The results of η and the calculated ionization energies are given in Table VIII. Despite the large η values required for these two sets of parameters, the calculated ionization energies are still in agreement with those in Table VII within 10%, which is a test of the validity of our approach. We note that, except the Mg and Si levels in the wurtzite GaN, the rest of the ionization energies in Table VII should be considered as the predictions from the present calculation.

TABLE VII. Calculated acceptor ionization energies E_A in both wurtzite and zinc-blende GaN (Ref. 17). Here η is the inverse hole mass factor as defined in the context. The energies E and the potential depth V_0 are in units of meV, and r_a, r_b, and r_1 are in units of Å. The experimental data E_{expt} and other theoretical results (Ref. 12) E_{theor} are also listed for comparison.

	Be	Mg	Ca	Zn	Cd	C	Si	Ge
r_a	1.06	1.40	1.74	1.31	1.48	0.77	1.17	1.22
r_b	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98
r_1	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68
V_0	1000	1300	1450	3400	4050	-8050	2050	2950
η	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07
E_A(wz)	187	224	302	364	625	152	224	281
E_{theor}	209	215	259	331		230	203	
E_{expt}	90	209		328	550		224	
	(Ref. 30)	(Ref. 33)		(Refs. 8 and 9)	(Ref. 6)		(Ref. 27)	
	160	224		340				
	(Ref. 31)	(Ref. 7)		(Ref. 6)				
	250	250						
	(Ref. 32)	(Ref. 6)						
E_A(bz)	183	220	297	357	620	143	220	276
E_{theor}	133	139	162	178		147	132	
E_{expt}		213						
		(Ref. 25)						
		224						
		(Ref. 26)						

IV. SUMMARY AND DISCUSSION

Since there is no *ab initio* theory that can calculate the acceptor ionization energies accurately, our empirical method seems to be a sensible and practical approach to this problem. As a result, we have a unified Hamiltonian that has embraced the overall experimental acceptor ionization energies for GaAs, GaP, InP, and GaN. Judging from the spread of the measured values in GaAs, GaP, and InP, our calculated acceptor ionization energies in GaN should be accurate to better than 10% and should have the correct chemical trend.

TABLE VIII. Calculated acceptor ionization energies E (in units of meV) in both wurtzite and zinc-blende GaN. The subscripts a and b indicate the results based on the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian parameters of Refs. 18 and 19, respectively. The inverse hole mass factor η used in each case is also given.

Impurity	E^a_{wz} ($\eta=1.35$)	E^b_{wz} ($\eta=1.67$)	E^a_{zb} ($\eta=1.18$)	E^b_{zb} ($\eta=1.43$)
Be	190	186	183	183
Mg	224	224	220	220
Ca	295	301	298	296
Zn	355	367	356	355
Cd	597	621	622	604
C	161	142	142	143
Si	225	225	220	220
Ge	278	284	276	276

We note that although our calculation method, namely the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian plus the impurity potential, is similar to that used by Mireles *et al.*,[12] our approach to the impurity potential and the mass parameters is quite different from theirs. Mireles *et al.*[12] took the impurity potentials to be the difference between the impurity and the host ionic pseudopotentials divided by the host dielectric constant. They calculated the acceptor levels for Be, Mg, Zn, Ca on the Ga sites and C and Si on the N site in GaN. For each acceptor, several sets of the available parameters for the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian were used. These different $\mathbf{k}\cdot\mathbf{p}$ Hamiltonians introduced a 50 meV uncertainty in the calculated ground state energies. Although their average ionization energies for the Ga-site acceptors (212, 223, 274, and 379 meV respectively for Be, Mg, Ca, and Zn) are not too different from our results, those for the N-site acceptors (241 and 210 meV respectively for the C and Si) are quite different from our calculated values of 152 and 224 meV, respectively. We note that their calculated ionization energies in C not only are higher than that for Be and Mg, but also are higher than those for Si, which reverse the chemical trend (C being the lowest) in all the systems studied here.

That C has a considerably smaller ionization energy than Mg is an important result. We found that this low ionization energy around 150 meV in wurtzite GaN was quite insensitive to the variation of the procedures used in the determination of the potential parameters. The simple reason behind this is that the C acceptor behaves like the hydrogenic acceptor in all the systems studied, as can been seen from a direct comparison of the experimental and calculated ionization energies of C in Tables IV–VIII with those in Table III for the hydrogenic model. In this connection, we note that the central-cell potential V_0 for C in Table VII has a different sign from other acceptors. The small ionization for C should give some hope for improving the *p*-doping efficiency in GaN. Even though C is amphoteric in nature,[28] strategy should be investigated to stabilize the C on the N sites. In terms of finding the shallower acceptors than Mg in GaN, Be seems to be the next choice. However, since Be is energetically more favorable to be an interstitial and donor rather than a substitutional impurity,[29] it may be difficult to make Be a useful acceptor.

The experimental study of the acceptor levels in GaN has been quite extensive. However, the measured ionization energies have large uncertainties. For example, the acceptor levels of 90,[30] 160,[31] and 250 (Ref. 32) meV for Be; 224 (Ref. 27) meV for Si; 209,[33] 224,[7] and 250 (Ref. 6) meV for Mg; 328 (Refs. 8 and 9) and 340 (Ref. 6) meV for Zn; and 550 (Ref. 6) meV for Cd have been measured for wurtzite GaN. The acceptor ionization energies of 213 and 230 meV in Mg-doped cubic GaN have also been deduced from very recent experiments.[25,26] A very low ionization energy (130 meV) was also reported for a resident impurity in zinc-blende GaN.[34] Considering the wide spread in the current experimental results, our predictions in Table VII should provide a useful reference for the acceptor ionization energies in both wurtzite and zinc-blende GaN.

V. CONCLUSION

In summary, we have investigated the chemical trend of acceptor levels in GaAs, GaP, InP, and GaN using the $\mathbf{k}\cdot\mathbf{p}$ theory and an empirical impurity potential model. A procedure for obtaining the parameters for the potential and the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian was developed from a systematic comparison of the calculations and experiments for GaAs, GaP, and InP. The procedure has produced accurate acceptor levels for GaAs, GaP and InP as compared with experiments. The procedure is then extended to predict the chemical trend of acceptor levels in both wurtzite and zinc-blende GaN systems. These results should provide a useful reference for the acceptor levels in GaN critically needed amidst the current widespread experimental and theoretical results. Our calculated results show that the acceptor ionization energies of C and Be (152 and 187 meV) in wurtzite GaN are lower than that of Mg (224 meV). This result should encourage a further investigation of the C and Be acceptors for possible improvement of the *p*-doping efficiency in GaN.

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[1] S. C. Jain, M. Wilander, J. Narayan, and R. Van Overstraeten, J. Appl. Phys. **87**, 965 (2000), and reference therein.

[2] S. J. Pearton, J. C. Zolper, R. J. Shul, and F. Ren, J. Appl. Phys. **86**, 1 (1999), and reference therein.

[3] D. Steigerwald, S. Rudaz, H. Liu, R. S. Kern, W. Götz, and R. Fletcher, JOM **49**, 18 (1997); W. Götz, N. M. Johnson, J. Walker, D. P. Bour, and R. A. Street, Appl. Phys. Lett. **68**, 667 (1996).

[4] K. H. Ploog and O. Bandt, J. Vac. Sci. Technol. A **16**, 1609 (1997).

[5] M. Ilegems and R. Dingle, J. Appl. Phys. **44**, 4234 (1973).

[6] S. Fischer, C. Wetzel, E. E. Haller, and B. K. Meyer, Appl. Phys. Lett. **67**, 1298 (1995), and references therein.

[7] M. Leroux, N. Grandjean, B. Beaumont, G. Nataf, F. Semond, J. Massies, and P. Gibart, J. Appl. Phys. **86**, 3721 (1999), and references therein.

[8] B. Monemar, H. P. Gislason, and O. Lagerstedt, J. Appl. Phys. **51**, 640 (1980).

[9] H. Y. An, O. H. Cha, J. H. Kim, G. M. Yang, K. Y. Lim, E. -K. Suh, and H. J. Lee, J. Appl. Phys. **85**, 2888 (1999).

[10] J. B. Xia, K. W. Cheah, X. L. Wang, D. Z. Sun, and M. Y. Kong, Phys. Rev. B **59**, 10 119 (1999).

[11] A. Baldereschi and N. O. Lipari, Phys. Rev. B **8**, 2697 (1973); **9**, 1525 (1974).

[12] F. Mireles and S. E. Ulloa, Phys. Rev. B **58**, 3879 (1998).

[13] G. L. Bir and G. E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, New York, 1974); G. E. Pikus, Zh. Éksp. Teor. Fiz. **41**, 1258 (1961) [Sov. Phys. JETP **14**, 898 (1962)]; **41**, 1507 (1961) [**14**, 1075 (1962)].

[14] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956); J. M. Luttinger and W. Kohn, *ibid.* **97**, 869 (1955).

[15] N. Binggeli and A. Baldereschi, Phys. Rev. B **43**, 14 734 (1991).

[16] P. Lawaetz, Phys. Rev. B **4**, 3460 (1971).

[17] K. Kim, W. R. L. Lambrecht, B. Segall, and M. van Schilfgaarde, Phys. Rev. B **56**, 7363 (1997).

[18] M. Suzuki, T. Uenoyama, and A. Yanase, Phys. Rev. B **52**, 8132 (1995).

[19] Y. C. Yeo, T. C. Chong, and M. F. Li, J. Appl. Phys. **83**, 1429 (1998).

[20] A.-B. Chen and P. Srichaikul, Phys. Status Solidi B **202**, 81 (1997).

[21] H. Wang and A.-B. Chen, J. Appl. Phys. **87**, 7859 (2000).

[22] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1960).

[23] An-Ban Chen and A. Sher, *Semiconductor Alloys: Physics and Material Engineering* (Plenum, New York/London, 1995).

[24] *Semiconductors-Basic Data*, edited by O. Madelung (Springer, Marburg, 1996), and references therein.

[25] D. P. Xu, H. Yang, D. G. Zhao, S. F. Li, and R. H. Wu, J. Appl. Phys. **87**, 2064 (2000).

[26] D. J. As, T. Simonsmerier, B. Schttker, T. Frey, D. Schikoar, W. Kriegeis, W. Burkhardt, and B. K. Meyer, Appl. Phys. Lett. **73**, 1835 (1998).

[27] J. Jayapalan, B. J. Skromme, R. P. Vaudo, and V. M. Phanse,

Appl. Phys. Lett. **73**, 1188 (1998).

[28] P. Bogusawski, E. L. Briggs, and J. Bernholc, Appl. Phys. Lett. **69**, 233 (1996).

[29] J. Neugebauer and C. G. Van Walle, J. Appl. Phys. **85**, 3003 (1999).

[30] F. J. Sánchez, F. Calle, M. A. Sanchez-Garcia, E. Calleja, E. Muñoz, C. H. Molloy, D. J. Somerford, F. K. Koschnick, K. Michael, and J. -M. Spaeth, MRS Internet J. Nitride Semicond. Res. **3**, 19 (1998).

[31] C. Ronning, E. P. Carlosn, D. B. Thomson, and R. F. Davis, Appl. Phys. Lett. **73**, 1622 (1998).

[32] A. Salvador, W. Kim, Ö. Aktas, A. Botcharev, Z. Fan, and H. Morkog, Appl. Phys. Lett. **60**, 2692 (1996).

[33] A. Kasi Viswanath, E. J. Shin, J. I. Lee, S. Yu, and D. Kim, J. Appl. Phys. **83**, 2272 (1998).

[34] D. J. As, F. Schmilgus, C. Wang, B. Schöttker, D. Schikoar, and K. Lischka, Appl. Phys. Lett. **70**, 1311 (1997).