HSE hybrid functional calculation of band gap deformation potential in MgGeN$_2$

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Abstract. The MgGeN$_2$ has been proposed as an alternative wide band gap semiconductor of III-N due to its flexibility in electronic property engineering. In this work, we calculated the relative deformation potential of band gap (a_g) in MgGeN$_2$ comparing with those in the well-known binary semiconductors such as GaN and ZnO which possess very close lattice parameters of MgGeN$_2$. The calculations were performed by using the density functional theory (DFT) with Heyd-Scuseria-Ernzerhof hybrid functional (HSE) approach. As the results, the a_g of MgGeN$_2$ is predicted as -5.37 eV, which is between those of GaN (-7.45 eV) and ZnO (-2.67). This a_g is useful for advanced study in band alignment, which is crucial quantity in all optoelectronic devices using semiconductor heterostructures.

1. Introduction

The wide band gap semiconductors in the group II-IV-N$_2$ have been studied in both theory and experiment, the band gaps of these compounds are found close to those of the famous III-N [1]. Moreover, the II-IV-N$_2$ has two different cations, so their electronic properties can be modified/tuned by varying the concentration of the group II or IV elements. From this ternary compounds, MgGeN$_2$ is an interesting one due to its direct band gap of 5.14 eV [1] which is suitable for high frequency optoelectronics application. To apply MgGeN$_2$ in real devices, similarly to normal semiconductors, we need to grow it on a substrate or create a heterostructure between it and its alloys or other semiconductors. Then, the structural distortion due to a lattice mismatch at the interfaces will occur and affect energy levels in the band structure such as valence band maximum (VBM), conduction band maximum (CBM) and also band gap (E$_g$)[2]. The energy level shift is very important to extract other electronic properties in heterojunction semiconductors and can be described by investigating the deformation potential (DP) of that particular level. Thus, in this work, we calculate the band gap deformation potential (a_g) of MgGeN$_2$ by using the density functional theory (DFT) and compared with those of the well-known wurtzite semiconductors such as GaN and ZnO. These binary semiconductors were chosen because of their very less lattice mismatch and very close band gaps to those of MgGeN$_2$.

2. Computational Details

All calculations were performed based on DFT frame work with pseudopotential approach as implemented in QUANTUM ESPRESSO package.The experimental crystal structures were considered as the equilibrium structure. The strained structures were defined as the optimal structures calculated from the local density approximation (LDA) with fhi98PP pseudopotential for ZnO and GaN, UltraSoft pseudopotential (USPP) for $MgGeN_2$, which normally gives less lattice parameters than experimental values. In order to get the accurate band gaps, the beyond LDA methods such as generalized gradient approximation (GGA) and Heyd-Scuseria-Ernzerhof hybrid functional (HSE) approach [3] were included. For HSE calculations, we used the optimized norm-conserving Vanderbilt pseudopotentials from D. R. Hamann [4]. The mixing parameters, α, used for HSE calculation are 0.25 (typical value) and 0.42 for $MgGeN_2$ while GaN and ZnO are 0.31 and 0.38 respectively [5]. All bulk calculations in this work were done using converged k-point $4 \times 4 \times 4$ and 80 Ry for cut-off plane wave energy. In this study, we assume that the deformation potential (DP) is in linear relation with the strain as $DP = dE/dln(V)$. The difference of any absolute energy levels of unstrained and strained compounds is defined as $dE = \Delta E$. The strain is in the form of $dV/V = dln(V) = \Delta ln(V)$. Therefore, we can extract the relative deformation potential of band gap from $a_g = \Delta E_g / \Delta ln(V)$.

3. Results and Discussions

The relaxed structures, which obtained from LDA are presented in table 1. Note that, the structure of $MgGeN_2$ can be viewed as a superlattice of wurtzite structure i.e. a = $\sqrt{3}$ a_w, b = $2a_w$ and c = c_w. The relative volume differences with respect to the experimental data are -2.066, -2.865 and -4.189 % for $MgGeN_2$, GaN and ZnO respectively. In this work, we choose the experimental volumes to be the equilibrium volumes and consider these LDA structures as strained structures. The band gaps of all structures calculated by GGA and HSE, comparing with the previous works, are listed in table 2. As usual, GGA calculations give smaller gaps, while HSE calculations give a good agreement with the experimental gaps of ZnO and GaN. However, the experimental band gap of $MgGeN_2$ have not been reported yet. Only the theoretical band gaps of $MgGeN_2$ was proposed at 5.14 eV by using QSGW calculation [1], which is higher than that of the HSE calculation. The deviation of the HSE from QSGW calculation might be from choosing the typical mixing parameter α as 0.25. D. H. Seo et.al have shown that using HSE to calculate band gaps of metal compounds, which contain valence electrons in d-orbital, the mixing parameter have to be optimized from typical value [6]. Thus, to obtain a more accurate band gap of $MgGeN_2$ by using HSE calculation, the mixing parameter may increase from 0.25 to 0.42. As seen in table 2., the band gaps of strained structures is clearly larger than those of equilibrium structures.

**Table 1.** Lattice parameters (Å) of $MgGeN_2$, GaN, and ZnO

| Compounds | Lattice parameter | | | | | |
| | strained(LDA) | | | unstrained(Expt.) | | |
	a	b	c	a	b	c
$MgGeN_2$	5.456	6.561	5.133	5.494[a]	6.611[a]	5.166[a]
GaN	3.155	-	5.147	3.189[b]	-	5.185[b]
ZnO	3.188	-	5.164	3.248[c]	-	5.203[c]

[a]Ref[7],[b]Ref[8],[c]Ref[9]

Table 2. relative deformation potentials of band gap (a_g) of MgGeN$_2$, GaN and ZnO (eV)

Compounds	a_g recent work HSE	GGA	a_g previous works LDA+U[d]	LDA[d]	Expt.	E$_g$ recent work HSE	GGA	previous works
MgGeN$_2$(α : 0.25)	-5.15	-3.99	-	-	-	4.15	2.98	5.14(cal.)[a]
MgGeN$_2$(α : 0.42)	-5.37		-	-	-	5.02		
GaN	-7.45	-6.40	-7.7	-7.0	-7.9[e]	3.29	1.97	3.51 (exp.)[b]
ZnO	-2.67	-1.46	-2.9	-1.7	-3.6[f]	3.32	0.87	3.3 (exp.)[c]

[a]Ref[1],[b]Ref[10],[c]Ref[11],[d]Ref[12],[e]Ref[13],[f]Ref[14]
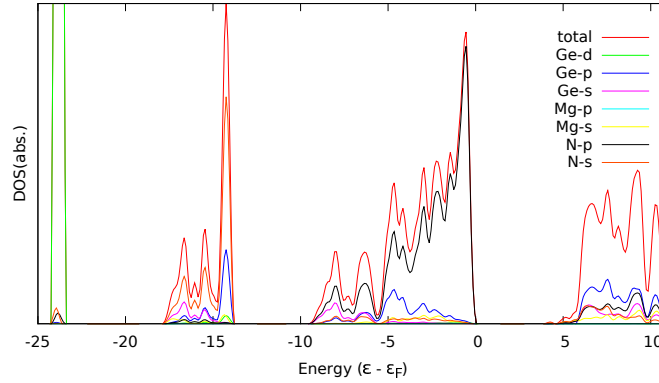
Figure 1. Partial density of state (PDOS) of MgGeN$_2$ (α : 0.25) obtained from HSE calculation

This is usual for normal semiconductors whose band gaps increase when the volumes decrease [15].The relative deformation potential of band gap (a_g) obtained from GGA and HSE were calculated as shown in table 2. As expected, the GGA underestimate a_g similarly to the results from LDA. In this work, we found that the HSE a_g of GaN and ZnO are close to those from LDA+U calculations and experiments. Furthermore, the a_g of MgGeN$_2$ is predicted as -5.37(α : 0.42). The dynamic of the energy levels can be explained by considering the electron couplings from cation and anion, which dominate mainly in the valence band and conduction band, in their partial density of state (PDOS). The explanation of energy level shift due to structural deformation is proposed by Wei et al. [16] i.e. the shifting of VBM and CBM due to the change of volume depends on kinetic energy, antibonding and bonding states. The kinetic energy increases with decreasing the volume so this shift the energy levels up. The bonding and anitbonding states cause the energy levels move down and up respectively. Therefore, in normal semiconductors, the magnitude of deformation potential in CBM (a_c) is larger than VBM (a_v) because of the shifted-up effects of the kinetic energy combining with antibonding state in conduction band. Moreover, the relation of a_c, a_v and a_g can be written as $a_g = a_c$ - a_v. In our cases, it can be observed that the magnitude of a_g in nitride-compounds (MgGeN$_2$ and GaN) are larger than that in oxide-compound (ZnO) .This result agrees with the previous calculation using LDA+U and LDA [12]. We can explain this in more details by separately considering the energy level changes into two cases. First, in the conduction band of these three compounds, the s-s and p-p antibonding in nitride compounds are stronger than that in oxide compound, (less

ionic characteristic). Then, the energy level shift up in CBM, a_c, of nitride-compounds is greater than that of ZnO. Second, in the valence band, we have to pay attention to the effect of p-d coupling since the cations e.g. Ga, Ge and Zn, might provide shallow electrons in d-orbital. This p-d coupling between cation and anion is considered as the antibonding state which can shift the energy level up compensating the shift-down effect from the existing p-p and s-p bonding states. As seen in PDOS, Zn-d orbital is dominate on the top of valence band [11], while Ga-d orbital[10] and Ge-d as shown in figure 1 are in deep shell. As the results of the combinations of antibonding, bonding states and the volume change, the energy shift down in VBM, a_v, in ZnO are smaller than those in GaN and MgGeN$_2$. Note that, in our study, when the systems are compressed the CBM shift up but the VBM shift down. Thus, from the discussion about a_c and a_v above, it declares that the magnitude of a_g in GaN and MgGeN$_2$ is larger than that of ZnO by reconsidering the relation a_v, a_c and a_g. Next, to compare a_g of GaN and MgGeN$_2$, the kinetic energy effect due to volume change need to be considered because their effects from bonding and antibonding state are similar. The equilibrium volume of both compounds in the orthorhombic structures, are 182.7 and 187.6 Å^3 for GaN and MgGeN$_2$ respectively. The magnitude of a_c in a smaller volume should be greater. Consequently, the magnitude of a_g of GaN is larger than that of MgGeN$_2$.

4. Conclusion

The band gaps and their relative deformation potentials, a_g, of MgGeN$_2$, GaN and ZnO were calculated using GGA and HSE approach.Only HSE band gaps of GaN and ZnO are in agreement with those from experiments. However, the band gap of MgGeN$_2$ obtained from HSE with the typical mixing parameter are smaller than QSGW E$_g$. The GGA a_g are close to LDA a_g while the HSE a_g of GaN and ZnO are consistent with LDA+U and experimental a_g. The a_g of MgGeN$_2$ is predicted as -5.37 eV. The magnitude a_g in nitride compounds are larger than that in oxide compound due to the weaker p-d coupling in valence band and less ionic behavior than those in oxide compound. Note that, in this study, the relation of absolute DP in CBM and VBM are assumed as a linear function of the strain. To obtain more accurate DP, the approximation beyond this relation such as lattice harmonic expansion should be included. The results of a_g reveal energy shift characteristic associated to volume deformation, which could be useful for designing semiconductor applications based on the group II-IV-N$_2$ compounds.

References
[1] Jaroenjittichai A P and Lambrecht W R 2016 *Phys. Rev.* B **94** 125201
[2] Colombo L, Resta R and Baroni S 1991 *Phys. Rev.* B **44** 5572
[3] Heyd J, Scuseria G E and Ernzerhof M 2003 *J. Chem. Phys* **118** 8207
[4] Hamann D R 2013 *Phys. Rev.* B **88** 085117
[5] Wang T, Ni C and Janotti A 2017 *Phys. Rev.* B **95** 205205
[6] Seo D H, Urban A and Ceder G 2015 *Phys. Rev.* B **92** 115118
[7] David J, Laurent Y and Lang J 1970 *Bull. Soc. Fr. Mineral. Cristallogr.* **93** 153
[8] Darakchieva V, Monemar B and Usui A 2007 *Appl. Phys. Lett.* **91** 031911
[9] Reeber R R 1970 *J. Appl. Phys.* **41** 5063
[10] Vurgaftman I and Meyer J R 2003 *J. Appl. Phys.* **94** 3675
[11] Srikant V and Clarke D R 1998 *J. Appl. Phys.* **83** 5447
[12] Janotti A and Van de Walle C G 2007 *Phys. Rev.* B **75** 121201
[13] Li S X, Wu J, Haller E E, Walukiewicz W, Shan W, Lu H and Schaff W J 2003 *Appl. Phys. Lett.* **83** 4963
[14] Mang A, Reimann K and Rubenacke S 1995 *Solid State Commun.* **94** 251
[15] Dalven R 1973 *Phys. Rev.* B **8** 6033
[16] Li Y H, Gong X G and Wei S H 2006 *Phys. Rev.* B **73** 245206