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Influence of hydrostatic pressure on the native point defects in wurtzite ZnO: Ab initio calculation

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ABSTRACT

The formation energies and transition energy levels of native point defects in wurtzite ZnO under applied hydrostatic pressure are calculated using the first-principle band-structure methods. We find that the pressure coefficient of the (2+/0) level for oxygen vacancy is larger than that of the (2+/1+) level for zinc interstitial, which demonstrates that the donor level of oxygen vacancy is deeper than that of zinc interstitial, therefore the latter is the more probable electron resource in native *n*-type ZnO. And the significantly different pressure dependence of the transition levels between them can be used to determine the origin of the green luminescence center in ZnO. Zinc octahedral interstitial and oxygen tetrahedral interstitial configurations became the dominant defects under 5 GPa at their favorable growth conditions, respectively. The formation of defects under applied pressure is the result of fine interplay between internal strains, charges on the defects and applied external pressures.

1. Introduction

Since ZnO has a direct band gap of 3.3 eV and a large exciton binding energy of 60 meV, it has been considered as a promising material for short wavelength optoelectronic device [1]. Despite its advantages, technological progress has been hindered by the lack of reliable *p*-type doping [2]. The main reason might be the incomplete understandings of doping and compensation mechanics in ZnO although a number of theoretical and experimental works have been conducted [3–7]. For example, on the dominate origin of the unintentional *n*-type conductivity in ZnO, a common opinion is that Zn-rich defects such as zinc interstitial (Zn_i) [8,9] or oxygen vacancies (V_O) [10,11] are shallow donors and a main source of electrons in as-grown materials. As for the blue–green emission, centered at around 500 nm in wavelength, it has been explained within the context of transitions involving self activated centers formed by a doubly ionized zinc vacancy (V_{Zn}) and an ionized Zn_i [12] and V_O [13,14]. Since the electrical and optical properties of a semiconductor are largely determined by the nature and number of its native defects and impurities, a fundamental understanding of them in ZnO is urgent for the development of *p*-type material. Experimentally, Deep Level Transient Spectroscopy (DLTS) is a unique and powerful tool for the study of electrically active defects (known as traps) in semiconductors based on the fact that the wave function of deep level defects is fairly delocalized and changes apparently relative to the band edge under applied pressure, while the shallow ones do not. Theoretically, we use the applied pressure as a probe of the properties of semiconductors as well as an engineering technique of defects in them, that is, through intentionally introduction of defects aiming to tune the material properties [15]. The pressure effect analysis is interesting because the direct comparison of experimentally obtained pressure dependence of the defect levels with theoretical results can be a very useful tool in identification and characterization of the defect states. And proper understanding of them allows for tuning the material properties by controlling the doping.

In the present work, we have calculated the pressure dependence of the formation energies and transition level of the native point defects in ZnO using the first-principle band-structure methods. And in the next section we describe the methods used in the calculation. The results of our calculation of defect formation volume, formation enthalpy, transition energy levels and our discussions are given in Section 3 and the Letter is concluded in Section 4.

2. Methods

To check the stability of native point defects under applied hydrostatic pressure, we performed formation energy calculation for different native point defects in wurtzite ZnO under 5 GPa, larger

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than which will transform ZnO from hexagonal to cubic structure [16]. Under conditions of constant temperature and pressure, the thermodynamic equilibrium state of a system is determined by the Gibbs free energy:

$$G = E - TS + PV = H - TS, \tag{2.1}$$

where E and H denote the internal energy and the enthalpy, T and S are the temperature and the entropy, and P and V represent pressure and volume, respectively. At 0 K and under ambient pressure, the change in volume when a defect is introduced into the system is relatively small, and in almost all the theoretical works carried out before, they focused only on computing the energy E. Once the pressure effect is taken into account, we must include the term PV, then the equilibrium properties of the system will be described by the enthalpy instead

$$H = E + PV. \tag{2.2}$$

Here $V = \partial H/\partial P$ is the formation volume and determines the pressure dependence of the formation enthalpy. Erhart et al. [17] have calculated the formation volume according to the formula in [18]. When the sample is applied hydrostatic pressure, the change of crystal volume is the result of internal strain from defect and external pressures:

$$V_D^f = V_T - V_P. \tag{2.3}$$

Here, V_T is the total volume change of the supercell containing defect under hydrostatic pressures. V_P is the volume change caused by external pressure and V_D^f is the change of ideal crystal volume when the defect is introduced into it under ambient pressure. Therefore, V_D^f should be a constant for specific defect and is a symbol of defect concentration dependent on pressure. While Tian et al. [19] have proved that the defect formation volume V_D^f changes with pressure and that might be because they treated the V_T as the formation volume of defect. All the enthalpy calculations for neutral and charged defects are carried out using the frozen-core projector-augmented-wave (PAW) [20] method within the density-functional theory (DFT), as implemented in the code *VASP* [21]. The Zn 3*d* electrons are explicitly treaded as valence electrons. The energy cutoff for the plane wave expansion is 400 eV. For exchange and correlation, the functional proposed by Perdew and Zunger was used, with the Perdew–Becke–Ernzerhof generalized gradient approximations (GGA) [22]. All the defect calculations were performed with 72-atom hexagonal supercells. For charged defects a homogeneous compensating background charge was added. In all calculations, the volumes are fully relaxed until the Hellmann–Feynman forces acting on the atoms become less than 0.01 eV/Å.

The formation enthalpy of defect D in charge state q is defined as:

$$H^f(D,q) = H(D,q) - H(\text{host}) + \sum_i n_i\mu_i + q\varepsilon_F, \tag{2.4}$$

where $H(D,q)$ is the enthalpy of the supercell with defect D in charge state q; H (host) is the enthalpy of the perfect supercell; n_i indicates the number of atoms i (Zn or O) that have been added to ($n_i < 0$) or removed ($n_i > 0$) from the supercell; μ_i is the chemical potential of species i referenced to the elemental solid (metal zinc)/gas (oxygen molecule) energy; q is the number of electrons transferred from the supercell to the reservoirs in forming the defect cells. ε_F is the Fermi level with respect to the valence-band maximum (VBM) and is aligned using the electrostatic potential away from the defect. Formula (2.4) indicates that the formation enthalpy and consequently the concentration of neutral defects depend on host-element chemical potentials μ_{Zn} and μ_O which are related to growth conditions [23]. However, the cation or anion chemical potential cannot be chosen freely. To keep ZnO thermodynamically stable, it is required that $\mu_O + \mu_{Zn} = \Delta H_f(\text{ZnO})$, where $\Delta H_f(\text{ZnO})$ is the formation enthalpy for bulk ZnO. Our calculated $\Delta H_f(\text{ZnO})$ equals -3.048 eV and is in good agreement with the experimental value -3.6 eV. In our calculation, we suppose that the pressure dependence of μ_O was negligible but that of μ_{Zn} was not [24].

Table 1
The formation volumes of point defect in ZnO under hydrostatic pressure of 5 GPa in the unit of volume formula unit. ("*t*" is the tetrahedral site and "*o*" is the octahedral one)

Defect	Charge state				
	−2	−1	0	+1	+2
V_{Zn}	0.683	0.333	0.149		
O_{Zn}	−0.105	0.238	0.571		
$O_i(t)$	0.491	0.143	−0.262		
$O_i(o)$	0.145	−0.150	0.47		
Zn_O			0.637	0.329	−0.233
$Zn_i(t)$			0.07	−0.314	−0.719
$Zn_i(o)$			−0.07	−0.324	−0.707
V_O			−0.467	−0.746	−1.07

3. Results and discussions

3.1. Formation volumes

The formation volumes of various native point defects including oxygen and zinc vacancies, interstitials and antisites under 5 GPa are given in Table 1 and shown as a function of charge state in Fig. 1. All defects exhibit a linear dependence on their charge states. While in Ref. [17], they found that oxygen vacancy behaves atypically with all the others in their calculation and the authors ascribed this to the different local relaxation between the neutral and positive charged states of Zn atoms surrounding the vacancy site, that is, in neutral state the Zn atoms relax outwards, while for positive charged states they moved inwards [6,7]. However, attention must be paid to the different conditions among our works that their nonlinear charge state dependence of the formation volume for V_O is its natural behavior under ambient pressure. When hydrostatic pressure is applied to the supercell containing the V_O which leaves large vacant space inside the crystal, the whole will contract regardless of their charge states. That is, the local relaxation characteristics are tuned by the application of pressure. Therefore the formation of native point defects is related to a fine interplay between internal strains, charges on the defects and applied external pressures [15].

3.2. Formation energies

Fig. 2 shows the calculated defect formation energies of the native point defects assuming their most favorable growth condition, i.e., the Zn-rich and O-rich limit at ambient pressure without corrections. The result is: Under O-rich condition, the zinc vacancies are the dominant defect type. Calculated with GGA + U, Ref. [17] proves the dumbbell interstitial oxygen ($O_{i,db}$) is also the dominant one when the Fermi level is approaching the VBM, which was not included in our calculations; Under Zn-rich condition, the oxygen vacancy is energetically slightly more favorable than Zn octahedral interstitial by about 0.6 eV lower in formation energy near the VBM and therefore is the most likely defect for all Fermi levels, consistent with all the other earlier studies [4,17].

The formation energies of Zn antisite (Zn_O), V_O, V_{Zn}, $Zn_i(o)$, and $Zn_i(t)$ under their favorable growth conditions as a function of the Fermi energy, for two values of hydrostatic pressure, $P = 0$ and 5 GPa were shown in Fig. 3. The changes in slope of the lines

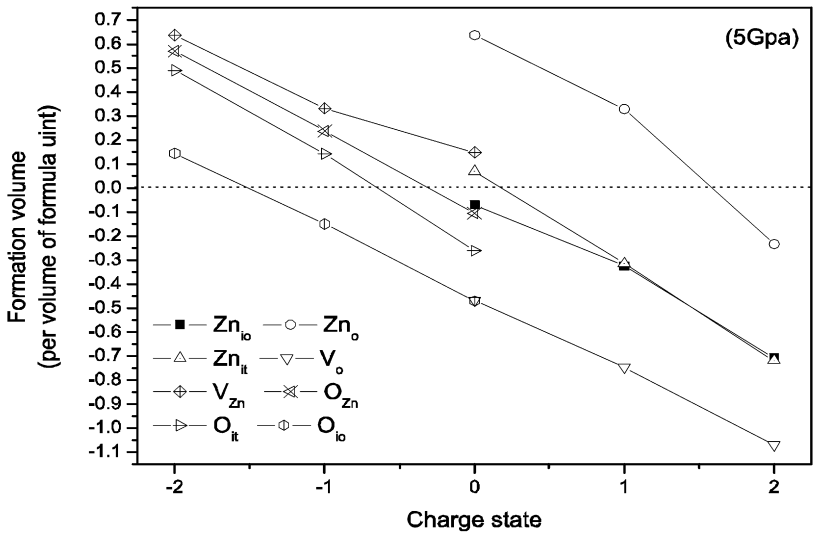

Fig. 1. Variation of defect formation volumes with charge state under 5 GPa in the units of volumes per formula. Symbol type and interior represent different defects, respectively.

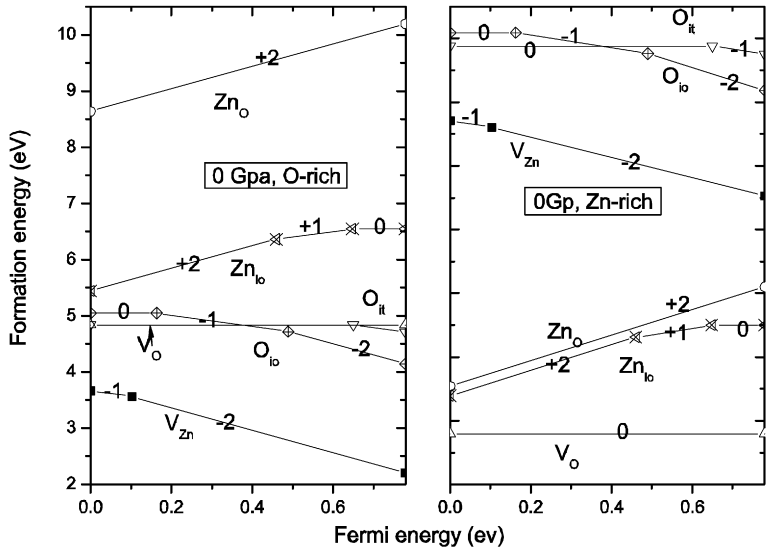

Fig. 2. Calculated defect formation energies are shown as a function of the Fermi energy E_f (within the region of GGA calculation) at the oxygen-rich (a) and zinc-rich (b) limits, respectively.

represent changes in the charge state of the defect, while the corresponding transition energy levels are marked with vertical lines. From Fig. 3(a) to (e), we observe the following results: The formation energies decrease with pressure for $Zn_i(o)$ and $O_i(t)$, but increase for V_O, Zn_O and V_{Zn} independent of their charge states. Quantitative difference can be seen from the values of the pressure coefficient of formation enthalpy and from their dependence on the charged states of the defects. It seems that the pressure dependence of the formation enthalpy could not be accounted for by the defect formation volume alone. As can be seen from Fig. 1 in our Letter and Fig. 3 in [17], for example, the formation volume of V_O is always negative for different charge states and under different pressures. Thus, according to $V = \partial H/\partial P$, when the crystal is under applied pressure, its formation enthalpy would decrease in principle, which contrasts our calculations. Therefore, we draw a conclusion that under applied hydrostatic pressure, the formation of native point defects is related to a fine interplay between internal strains, charges on the defects and applied external pressures.

In Figs. 2, 3 and 4, the Fermi level ε_F varies from the VBM to the conduction-band maximum (CBM) that is in the region of the band gap E_g. However, the GGA calculation usually underestimates E_g as compared with experimental data. Our calculated E_g value at Γ point of ideal ZnO is 0.779 eV under 0 GPa, and 0.831 eV under 5 GPa, which agrees well with the conclusion that the E_g blue shifts under applied pressure below the phase transition pressure from the wurtzite to cubic NaCl structures [25]. The experimental E_g value under ambient pressure is 3.37 eV and according to the pressure coefficient of band gap from Ref. [25], we got the experimental value 3.67 eV under 5 GPa. The difference between theoretical and experimental values (ΔE_g) could affect the formation energies of intrinsic defects in ZnO. When a defect introduces extra occupied levels below CBM, which are composed of cation orbital similar to the conduction band, its formation energy will be underestimated since the energy position of the CBM itself is underestimated. To correct the well-known band gap error effect on the formation energies of donors, we assume a crude correction that the conduction band is rigidly shifted upward to match the experimental E_g. Then the formation energies for defects that have donor characters are corrected by adding a value of $n \times \Delta E_g$, where n is the number of electrons at defect-induced

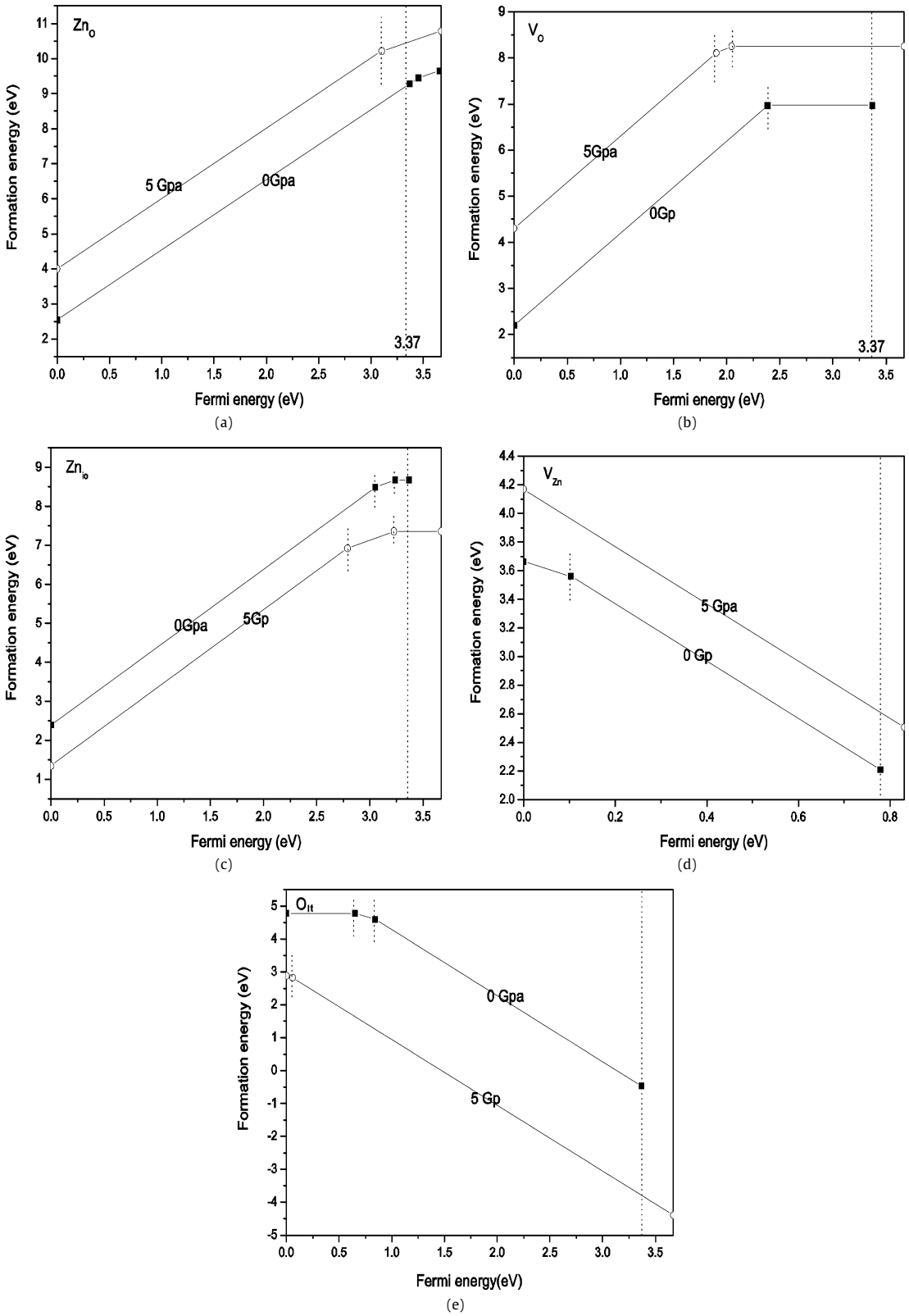

Fig. 3. Formation enthalpies of selected defect (a)–(e) assuming their most favorable growth conditions are shown as a function of the Fermi energies for hydrostatic pressure 0 and 5 GPa.

levels in E_g. Because of the fact that the energy level $\varepsilon(q/q')$ is defined as the E_f where the formation energy of defect α in charge state q equals to that in charge state q'. Such corrections on formation energy also corrected the ionization energy levels of donors in band gap. Fig. 4(b) is the corrected results for those defects that exhibit donor characteristics. As it shows, in n-type materials where the Fermi level is positioned high in the band gap, the $\mathrm{Zn}_i(o)$ has the lowest formation energy and becomes the dominant defects compared with the ambient condition where V_{O} is abundant. Therefore, we conclude that under zinc-rich condition

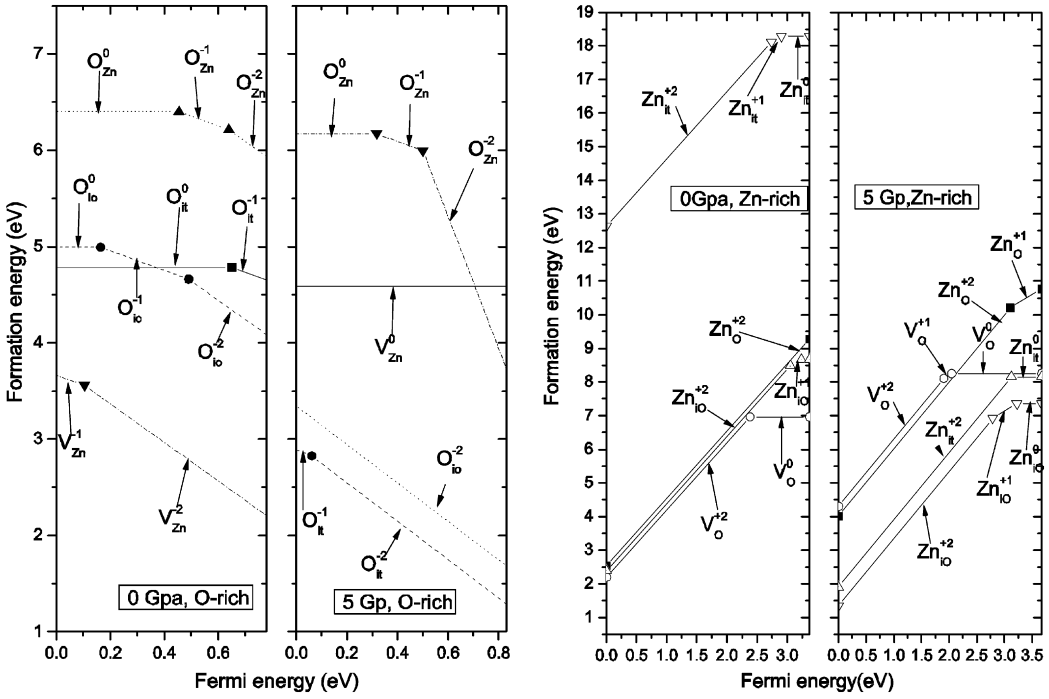

Fig. 4. Comparisons of formation energy of the selected defects under their favorable growth condition between 0 GPa and 5 GPa.

Table 2
The defect transition energy levels under 0 GPa and 5 GPa in eV

	Donors with respect to E_{CBM}			Acceptor with respect to E_{VBM}		
	(2+/1+)	(1+/0)	(2+/0)	(0/1−)	(1−/2−)	(0/2−)
V_O	−1.06[a]	−0.905	−0.983			
	−1.768[b]	−1.624	−1.169			
$Zn_i(o)$	−0.284	−0.129	−0.224			
	−0.871	−0.445	−0.663			
$Zn_i(t)$	−0.628	−0.462	−0.545			
	−0.275	−0.805	−0.56			
Zn_O	0.084	0.286	0.185			
	−0.567	0.291	−0.319			
V_{Zn}				−0.172	0.103	−0.0345
				−0.338	−0.543	−0.441
$O_i(o)$				0.163	0.490	0.653
				−0.476	−0.203	−0.670
$O_i(t)$				0.650	0.840	1.490
				−0.154	0.06	−0.094

[a] 0 GPa. [b] 5 GPa.

and under higher pressure, it is unfeasible to turn the material into p-type by intrinsic defects, because interstitial zinc appears as dominant defects with lower thermal ionization energy besides hydrogen interstitial, if it exits beforehand. For the defects that have acceptor characteristics as shown in Fig. 4(a), we did not apply the corrections mentioned above to them, because such underestimation of band gap has minimum effect on them as shown in Ref. [3]. We only care about their relative position to the VBM. From Fig. 4(a), we can see that almost all the transition levels are outside the band gap, except the transition energy level $\varepsilon(-1/-2)$ of $O_i(t)$. And under 5 GPa, the $O_i(t)$ became the abundant defects instead of V_{Zn} at 0 GPa, and it is a shallower acceptor with $(-1/-2)$ locating at 60 meV above VBM (see Table 2). Meanwhile, the O-rich condition is not the favorable formation condition for the hole killers such as V_O and Zn_O besides the fact that under 5 GPa applied pressure the formation of V_O and Zn_O increased and for $Zn_i(o)$ as it has the characteristics of CBM, the formation energy correction scheme increased its formation values despite that it is a shallow donor. Therefore, the behavior of $O_i(t)$ under applied pressure and oxygen-rich condition exert hope for those trying to make ZnO p-type without intentional dopant.

3.3. Defect electronic transition levels

Table 2 lists the defect transition energies of all the defects considered between their different charged states under ambient pressure and 5 GPa applied pressures. For donors, transition energy levels are given with respect to CBM and the negative values mean inside the band gap. While the acceptors levels are given with respect to the VBM, and the positive values mean inside the band gap. It is suggested experimentally that V_O is the main source of intrinsic n-type conductivity [26], while nonlinear spectroscopy measurements showed that the donor level locates at 1.2 eV above the VBM [27]. In fact, we find that the (2+/0) transition level of V_O lies at 0.983 eV below the CBM, which is similar to Zhang et al. [4] who have performed the SIC calculations for ZnO, and found that the single-particle defect levels of the neutral V_O is positioned at 1.0 eV below the CBM, close to our GGA calculation. Under applied pressures, the pressure coefficients of transition energy levels demonstrate the defect characteristics of deep or shallow levels. For oxygen vacancy, all the pressure coefficients of the energy levels are large and positive without special dependence on its charge state, demonstrating a strong dependence on pressure. In contrast, for zinc interstitial, no matter tetrahedral or octahedral configurations, their pressure coefficients are relative small compared with the oxygen vacancy, especially for tetrahedral interstitial zinc, where its (+1/+2) decreases with increased pressure. The same trend is also found for Zn antisites. All of these demonstrate that V_O is a deep level, while the Zn_i is a shallow one, and this phenomenon can be used to identify the deep level characteristics of oxygen vacancy. Therefore, we draw a conclusion that V_O is not the source of electrons in native ZnO and zinc interstitial might be the origin, but we could not exclude the interstitial H, which is not included in our calculation. The significant difference between the pressure dependence of the transition levels for the

two dominant donor defects (V_O, Zn_i) suggests that the controversy with regard to the green luminescence center in ZnO [12–14] could be resolved by performing pressure-dependent experiments.

4. Conclusions

As a probe and engineering technique, pressure is a useful tool in identification and characterization of the defect states in ZnO. Our first-principle total-energy calculations indicate that the pressure coefficient of the level $(2+/0)$ for oxygen vacancy is larger than that of the $(2+/1+)$ for zinc interstitial and this demonstrates that oxygen vacancy is deeper than zinc interstitial. The significantly different pressure dependence of the transition levels between V_O and Zn_i can be used to determine the origin of the green luminescence center in ZnO. When applied hydrostatic pressure, zinc octahedral interstitial and oxygen tetrahedral interstitial became the dominant defects under zinc and oxygen-rich condition, respectively. The formation of defects under applied pressure could not be accounted for by formation volume alone, and it is related to a fine interplay between internal strains, charges on the defects and applied external pressures.

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