

Reversing doping asymmetry in semiconductor thin films with external voltage

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Doping asymmetry is a notable phenomenon with semiconductors and a particularly long-standing challenge limiting the applications of most wide band-gap semiconductors, which are inherent of spontaneous heavy *n*- or *p*-type doping because of their extreme band edges. This study theoretically shows that by applying a proper external voltage on materials during their growth or doping processes, we can largely tune the band edges and consequently reverse the doping asymmetry in semiconductor thin films. We take zinc oxide as a touchstone and computationally demonstrate that this voltage-assisted doping approach efficiently suppresses the spontaneous *n*-type defects by around four orders under three distinct growth conditions and successfully generates *p*-type zinc oxide up to the lowest acceptor levels. The proposed approach is insensitive to materials, growth conditions, or defects origins, and thus offers a general solution to the doping asymmetry in semiconductor thin films.

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I. INTRODUCTION

Wide band-gap (WBG) semiconductors possess a broad range of fascinating applications [1–3], such as blue lasers, high-power/high-temperature/high-frequency devices, transparent electrodes, and potentially room-temperature spintronics. However, decades of studies have clearly demonstrated that most WBG semiconductors are inherent in spontaneously forming heavy *n*- or *p*-type doping and meantime suffer from overwhelming difficulties to achieve the opposite doping type [4–6]. This phenomenon is known as the doping asymmetry, which renders an ideal design based on the homojunctions of WBG semiconductors unreachable and is particularly unfortunate for those with wafer-size single crystals, such as ZnO and Ga₂O₃. The doping asymmetry originates from the fact that a wide band gap usually means either a very high conduction-band maximum (CBM), e.g., -0.2 eV for diamond [7,8], or a very low valence-band maximum (VBM), e.g., -7.8 eV for ZnO and -8.9 eV for Ga₂O₃ [9,10], which renders the formation of *n*-type or *p*-type defects thermodynamically unfavorable and the corresponding ionization energy levels relatively deep in the band gap. Such feature is clearly shown in Fig. 1, which compares band edges among the typical spontaneous *n*- or *p*-type WBG semiconductors and conventional semiconductors [11,12]. The only two commercialized WBG semiconductors, GaN and SiC, fortunately possess band edges close to those of GaAs and Si. These extreme band edges are intrinsic with WBG semiconductors and thus explain their long-standing doping asymmetry.

According to the defect thermodynamics, the concentrations of charged defects in crystals are governed by the Fermi

energy and the chemical potentials under specific growth conditions [13,14]. The two factors are typically coupled through the charge-neutrality condition and the defect concentrations can be determined solely by the growth conditions. Because of the narrow optimal growth windows and the compensation effects of spontaneous defects [15–17], traditional attempts to achieve the nonspontaneous doping type by changing growth conditions have achieved very limited success [18]. In this study, we propose to tune the defect thermodynamics by relatively shifting the band edges of semiconductors using external voltages during the growth or doping processes. We derive the theoretical formula of this approach, propose a schematic device, and choose ZnO as a classical example to demonstrate this approach using first-principles calculations. Our results reveal distinct defect origins of the spontaneous *n*-type doping for three representative growth methods of ZnO and the proposed voltage-assisted doping approach successfully generates *p*-type doping up to the lowest acceptor level.

II. METHODS

All the first-principles calculations in this work were based on the density-functional theory (DFT), as implemented in the Vienna *ab initio* Simulation Package [19]. We adopted the exchange-correlation functional of Heyd-Scuseria-Ernzerhof (HSE06) [20] as well as the Hubbard model with an effective *U*-*J* value of 6 eV for the 3*d* electrons in Zn. This approach gives an overall excellent description of the lattice parameters, band gap, and formation energy of ZnO bulk [21]. By contrast, the typical method of using HSE functional with 36% of Hartree-Fock exact exchange overestimates the formation energy of ZnO bulk by 22% [21]. To describe the special relativity effects in Pb, the spin-orbit coupling is included for the relevant calculations. A plane-wave energy cutoff of 435 eV was used,

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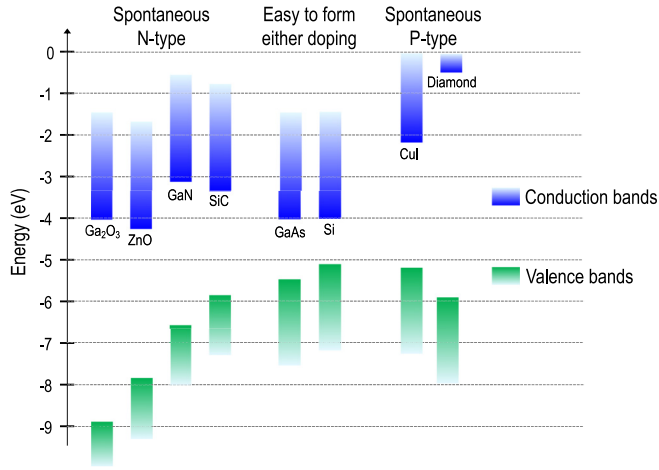


FIG. 1. Band edges of typical WBG semiconductors and those of conventional semiconductors relative to vacuum level. Original data were obtained from literature [7,8].

together with following projector augmented-wave potentials: Zn_GW ($3d^{10} 4p^2$) for Zn, O_s_GW ($2s^2 2p^4$) for O, H_GW ($1s^1$) for H, N_GW ($2s^2 2p^3$) for N, P_GW ($3s^2 3p^3$) for P, As_GW ($4s^2 4p^3$) for As, Ag_GW ($5s^1 4d^{10}$) for Ag, and Pb_sv_GW ($5s^2 6s^2 5p^6 6p^2 5d^{10}$) for Pb. The Brillouin zone was sampled with a $2 \times 2 \times 2$ gamma-centered mesh.

A 72-atom supercell of wurtzite ZnO is used to simulate 38 defects in total, including 7 native point defects: Oxygen and zinc vacancies (V_O and V_{Zn}), interstitials (O_{i1} , O_{i2} , and Zn_i), and antisites (O_{Zn} and Zn_O); 8 native pair defects: $V_O + V_O$, $V_{Zn} + V_{Zn}$, $V_O + O_i$, $V_{Zn} + Zn_i$, $V_O + V_{Zn}$, $V_O + O_{Zn}$, $V_O + Zn_i$, and $V_O + ZnO$; 7 H-related defects: H_{Zn} , H_O , H_i , $V_{Zn} + 2H$, $H_i + O_{Zn}$, $H_i + V_{Zn}$, and $H_i + O_i$; 2 defects related to the impurity lead: Pb_{Zn} and $Pb_{Zn} + V_O$; and 14 defects related to the typical p -type dopants: N_i , N_{Zn} , N_O , $N_{Zn} + V_{Zn}$, $N_{Zn} + 2V_{Zn}$, P_O , P_{Zn} , As_O , As_{Zn} , $As_{Zn} + V_{Zn}$, $As_{Zn} + 2V_{Zn}$, Ag_i , Ag_{Zn} , and $Ag_{Zn} + V_O$. These defects are chosen with consideration of the known defect types, the dominant impurities in the examined growth methods, and the typical dopants. Symmetry is broken to allow a possible Jahn-Teller distortion around the defects. The *ab initio* method proposed by Freysoldt, Neugebauer, and Van de Walle (FNV correction) is adopted to reduce the image charge interaction and adjust the potential alignment between the perfect and defected structures [22,23]. Our tests indicate that the error in defect-formation energy after the FNV correction is limited to ~ 0.1 eV [21]. Table I summarizes the typical growth conditions and the corresponding chemical potentials for the molecular-beam epitaxy (MBE) [24], hydrothermal growth (HTG) [18,25,26], and pressurized melt growth (PMG) [27,28] of ZnO.

III. RESULTS AND DISCUSSIONS

In this study, we first lay a theoretical foundation of tuning the defect thermodynamics using external voltage. After that, we computationally examine the point defects in ZnO bulk grown by MBE, HTG, or PMG, and reveal the defect origins of the spontaneous n -type doping. Then, we apply our voltage-

TABLE I. Experimental growth temperature, T_G , partial pressure of oxygen, P_{O_2} , partial pressure of water vapor, P_{H_2O} , and concentration of lead impurity for the MBE, HTG, and PMG of ZnO, and corresponding chemical potentials used in this work. Chemical potentials for Zn-rich and O-rich conditions are given for comparison; all growth conditions are organized in decreasing Zn chemical potential.

	Zn rich ^b	MBE ^c	HTG ^d	PMG ^e	O rich ^b
T_G (K)		692	~ 650	2200	
P_{O_2} (atm)		1.3×10^{-7}	$\sim 5 \times 10^{-31}$	~ 50	
P_{Zn} (atm)		2×10^{-4}			
P_{H_2O} (atm)			~ 1085		
Pb (cm^{-3})				$\sim 3.6 \times 10^{17}$	
N (cm^{-3})	$\sim 10^{12}$		$\sim 10^{12}$	$\sim 10^{12}$	
μ_{Zn} (eV)	-0.70	-1.10	-1.98	-3.51	-4.16
μ_O (eV)	-10.60	-8.03	-9.46	-9.18	-7.14
μ_H (eV)			-4.09		
μ_N (eV) ^a		-5.48	-4.32	-8.97	
μ_{Pb} (eV) ^a				-7.87	

^a μ_N and μ_{Pb} are evaluated self-consistently, so the total content of N and Pb equals $\sim 10^{12}$ and $3.6 \times 10^{17} cm^{-3}$, respectively.

^b μ_{Zn} under Zn-rich condition equals the total energy per atom of Zn metal and μ_O under the O-rich condition corresponds to the total energy per atom of O_2 molecule; the equilibrium condition of $\mu_O + \mu_{Zn} = \mu_{ZnO}$ is used to obtain the other chemical potential under the same condition, where μ_{ZnO} is the energy per formula of ZnO bulk.

^c μ_{Zn} and μ_O are Gibbs free energy per atom of the Zn and O_2 beams, respectively.

^d μ_H and μ_O , respectively, correspond to free energy per atom of H_2 and O_2 under equilibrium conditions of water decomposition at 650 K and 1085 atm. μ_{Zn} is calculated using equilibrium condition of $\mu_O + \mu_{Zn} = \mu_{ZnO}$ at 650 K.

^e μ_O is Gibbs free energy of O_2 per atom under experimental conditions and μ_{Zn} is calculated using equilibrium condition of $\mu_O + \mu_{Zn} = \mu_{ZnO}$ at 2200 K.

assisted doping approach to the different growth methods of ZnO bulk and demonstrate its effectiveness of reversing the doping asymmetry. Finally, we propose an experimental device to realize the voltage-assisted doping approach.

A. Theoretical model of the voltage-assisted doping approach

Our start point is the classical definition of formation energy for a dilute point defect A_B^q , as illustrated in Eq. (1) [13,14]:

$$E_f(E_F) = E_{tot}(A_B^q) - E_{tot}(\text{perfect}) + \mu_B - \mu_A + q(E_{VBM} + E_F), \quad (1)$$

where A_B^q refers to a defect with element A occupying a lattice site B and possessing a charge state q ; $E_{tot}(A_B^q)$ and $E_{tot}(\text{perfect})$ are the total energies of systems with the charged point defect and the perfect crystal, respectively. μ_A and μ_B are the chemical potentials of element A and B under experimental conditions, respectively. E_{VBM} is the VBM energy in perfect crystal, and E_F is the Fermi level relative to E_{VBM} . In a supercell calculation, an extra term to correct the finite-size errors for charged defects [22,23] should be added to $E_{tot}(A_B^q)$.

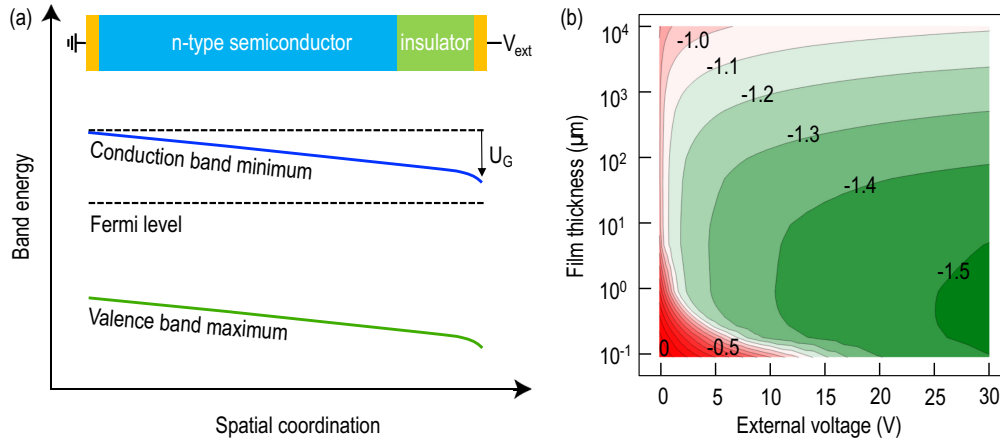


FIG. 2. (a) Schematic spatial dependence of band edges in an n -type semiconductor thin film under a positive external voltage. Inset shows a schematic device. (b) External voltage-induced band bending for n -type ZnO films with donor concentration of 10^{14} m^{-3} at 650 K, which is a lower border of growth temperatures of ZnO. Labels around contours are in unit of eV.

The last term of Eq. (1) explains why the extreme band edges of WBG semiconductors (Fig. 1) can easily lead to the doping asymmetry.

In this study, we propose to tune the band edges of semiconductors using an external voltage. Figure 2(a) schematically shows the critical energy levels of an n -type semiconductor thin film under a positive external voltage for the model in the inset. The spatial distributions of electrostatic potential, Fermi level, and band edges in the model can be solved using Gaussian's law, with consideration of the dopant concentrations and free-charge carriers [29]. The ground terminal is subject to the Dirichlet boundary condition, while the insulator/semiconductor interface adheres to the continuity of electric displacement field. Numerical simulations with the COMSOL package [30] indicate that excess electrons can accumulate in the high-potential region and induce a downward band bending, namely $U_G \equiv E_{\text{CBM}}(V_{\text{ext}}) - E_{\text{CBM}}(0)$. Detailed examination of n -type ZnO films with different thickness and donor concentrations reveals that under the high growth temperatures of ZnO, U_G can be tuned till the Fermi level touches the CBM of ZnO, and the largest magnitude is about 1.5 eV [Fig. 2(b)] or nearly half of the band gap [21].

With such band bending, charged defects will gain new equilibrium distributions. For instance, the downward band bending in Fig. 2(a) will promote negatively charged or p -type defects but depress the positively charged or n -type defects. Quantitatively, the electrostatic energy of defect A_B^q changes by $-qU_G$, where the minus sign is added because U_G is referenced to electrons. The energies of perfect bulk, chemical potentials, and Fermi level, however, remain unchanged. Therefore, the total change of defect-formation energy under the band bending equals $-qU_G$ and the defect-formation energy is updated from Eq. (1) to Eq. (2):

$$E_f(E_{\text{FG}}, U_G) = E_{\text{tot}}(A_B^q) - E_{\text{tot}}(\text{perfect}) + \mu_B - \mu_A + q(E_{\text{VBM}} + E_{\text{FG}} - U_G), \quad (2)$$

where E_{FG} is the Fermi level under the gated voltage. Since Eq. (2) is mathematically equivalent to shifting the E_{VBM} in Eq. (1) by $-U_G$, the defect-formation energy curves based

on Eq. (2) can be obtained by shifting the E_{VBM} for the curves based on Eq. (1).

With the defect-formation energy, the corresponding defect concentration can be calculated through Eq. (3):

$$c(T_G, E_{\text{FG}}, U_G) = n_0 e^{-E_f(E_{\text{FG}}, U_G)/(k_B T_G)}, \quad (3)$$

where n_0 is the number density of potential defect sites and k_B the Boltzmann constant. The only variable in Eqs. (2) and (3) that cannot be easily obtained is E_{FG} , which, however, can be solved self-consistently according to the neutrality requirement, namely that the charges of all defects and free-charge carriers add up to zero, as shown in Eq. (4):

$$n_h(T_G, E_{\text{FG}}) - n_e(T_G, E_{\text{FG}}) + \sum_{\text{defect}} c(T_G, E_{\text{FG}}, U_G) q(E_{\text{FG}}, U_G) = 0. \quad (4)$$

Here, n_h and n_e are the density of free holes and electrons, respectively; T_G is the growth temperature; $q(E_{\text{FG}}, U_G)$ is the defect charge state; $c(T_G, E_{\text{FG}}, U_G)$ is the defect concentration. It is worth pointing out that solving Eq. (4) at T_G is critical to obtain the correct defect concentrations, because the high growth temperatures can dramatically impact E_{FG} .

When the external voltage is removed and temperature is reduced after growth or doping, the defect concentrations are expected to be largely frozen to the values under T_G and U_G . However, the defect charge states, the concentrations of free charge carriers, and the Fermi level are supposed to reequilibrate at the after-growth or after-doping temperature, T_{AG} . Therefore, the charge-neutrality condition at T_{AG} as expressed in Eq. (5) should be executed:

$$n_h(T_{\text{AG}}, E_{\text{FAG}}) - n_e(T_{\text{AG}}, E_{\text{FAG}}) + \sum_{\text{defect}} c(T_G, E_{\text{FG}}, U_G) q(E_{\text{FAG}}) = 0, \quad (5)$$

where E_{FAG} and $q(E_{\text{FAG}})$ are the self-consistent Fermi level and defect charge state at the temperature of T_{AG} without external voltage.

The above voltage-assisted doping approach exhibits two favorable advantages. First, this approach is insensitive to

the atomic composition of defects and growth conditions, because all the spontaneous donors or acceptors possess the same charge sign and thus undergo the same qualitative change by external voltage. Second, the external voltage can tune the defect-formation energies without changing other growth conditions, such as growth temperature and precursors. By contrast, the traditional methodology of tuning the defect-formation energies by chemical potentials is largely limited by the optimal growth window.

B. Analyses of doping asymmetry in ZnO

To verify the proposed approach, we choose ZnO as a touchstone, which is known for spontaneous heavy n -type doping [6,31,32], has abundant experiments for verification, and possesses wafer-size single crystals and versatile potential applications [33,34]. We carry out first-principles calculations of defect thermodynamics based on the density-functional theory and closely examine three representative growth methods of ZnO. The first is the MBE, which involves a growth temperature of ~ 690 K, possesses extremely low impurities in high vacuum, and very low oxygen partial pressure of $\sim 1.3 \times 10^{-7}$ atm [24]. The second is the HTG, which is carried out at ~ 650 K and involves ZnO solute in water under a vapor pressure of ~ 1085 atm [25]. In this case, water decomposition into hydrogen and oxygen should be considered. The third is the PMG, which involves melting and crystallization of ZnO at ~ 2200 K under a high oxygen partial pressure of ~ 50 atm [27]. It has been found that metal impurities, such as Pb, Cd, and Fe, exist in the final crystals. See more details in Methods, Sec. II.

Figure 3 shows the defect-formation energies without external voltage for the relevant point and pair defects in ZnO under the MBE, HTG, and PMG conditions. Under the growth temperature of 692 K, ZnO crystal grown by MBE is only lightly n -type doped with a Fermi level 1.85 eV above the VBM, as shown in Figs. 3(a) and 3(b). The dominant donor is Zn_i^{2+} with a concentration of $1.5 \times 10^{11} \text{ cm}^{-3}$, comparable to the free electron and hole concentrations of 2.9×10^{11} and $1.7 \times 10^{10} \text{ cm}^{-3}$, respectively. When the temperature is reduced to the after-growth temperature of 300 K, the free holes are dramatically reduced to almost zero ($4.6 \times 10^{-30} \text{ cm}^{-3}$), but the concentrations of Zn_i^+ and free electrons are largely frozen to their values at 692 K. This phenomenon finally leads to a significantly increased Fermi level of 2.94 eV, which corresponds to a strong n -type doping. Therefore, the n -type doping in the MBE-grown ZnO is not only caused by the Zn-rich growth condition (see Table I in Methods, Sec. II), but also because the high growth temperature leads to a Fermi level around midgap, which intrinsically favors/disfavors the formation of donors/acceptors.

Figures 3(d) and 3(e) show that the ZnO crystal prepared by HTG is also a strong n -type semiconductor, with an after-growth Fermi level at 3.01 eV above VBM, and thus confirms the experimental findings [26,35]. Different from the high-purity reactants in the MBE, the hydrogen impurities H_i^+ and H_O^+ , with a respective concentration of 3.2×10^{12} and $6.6 \times 10^7 \text{ cm}^{-3}$, dominate the spontaneous n -type doping in the HTG. Other major defects include $(\text{V}_{\text{Zn}} + 2\text{H})^0$, V_O^0 , and H_{Zn}^- . Because hydrogen is ubiquitous for the HTG, reduction

of the hydrogen-related donors is quite challenging under the typical growth conditions.

Unlike the MBE and HTG, the PMG involves a high oxygen partial pressure of ~ 50 atm and a high growth temperature of ~ 2200 K. Also, it has been reported that Pb and other impurities exist in the ZnO source material at a high level of ~ 5 ppm ($3.6 \times 10^{17} \text{ cm}^{-3}$) [27]. With consideration of the Pb-related defects, the Fermi level at the after-growth temperature is predicted to be 3.00 eV above VBM, as shown in Figs. 3(g) and 3(h), which explains the strong n -type doping effect in this growth method, too [36]. The major donor is found to be $(\text{Pb}_{\text{Zn}} + \text{V}_\text{O})^{2+}$, with a concentration of $2.9 \times 10^{16} \text{ cm}^{-3}$. Other dominant defects include Pb_{Zn}^0 , V_O^0 , $(\text{V}_\text{O} + \text{V}_{\text{Zn}})^0$, and $\text{V}_{\text{Zn}}^{2-}$. If we simply take out the Pb impurity, the after-growth Fermi level changes to 2.03 eV, suggesting that reduction of Pb and other similar impurities will help mitigate the n -type doping in the PMG.

The above results clearly show that the dominant spontaneous donors vary significantly with the growth methods of ZnO. The native defect Zn_i under the Zn-rich condition, the H-related defects from the water environment, and the metal impurities are responsible for the MBE, HTG, and PMG, respectively. We notice that H-related defects were suggested to be donors in ZnO from a general viewpoint without consideration of the growth conditions [37], and the other spontaneous donors mentioned above were totally missed, probably because of two reasons. First, the specific growth conditions were not considered in most previous predictions [38]. Second, the self-consistent determination of Fermi level with consideration of the growth and after-growth temperatures was not executed in literature.

Our calculations further indicate that p -type doping of ZnO without suppressing the abundant spontaneous donors is unlikely to succeed. Figures 3(c), 3(f), and 3(i) show the defect formation energies related to nitrogen [31,39–42]. We find that with the exactly same non-N defects, the N-doped ZnO still exhibits strong n -type doping, with a Fermi level of 2.90, 3.00, and 3.00 eV above the VBM for the MBE, HTG, and PMG, respectively. The effect of nitrogen doping is almost negligible for all these growth methods and thus explains the unsuccessful p -type doping of ZnO with N [43]. Other p -type dopants, including P, As, and Ag, behave similarly as N [21].

C. Application of voltage-assisted doping approach to ZnO

We now employ the voltage-assisted doping strategy to suppress the spontaneous donors and, meanwhile, enhance the acceptors in ZnO grown by the three types of experiment. Figure 4(a) shows that a U_G of about -1.2 eV brings down the Fermi level from 2.94 to 1.85 eV above VBM for the MBE. Meanwhile, the dominant donor Zn_i is dramatically reduced from 1.5×10^{11} to $\sim 1 \text{ cm}^{-3}$, together with an increase of acceptor O_i from $\sim 10^{-5}$ to $\sim 0.1 \text{ cm}^{-3}$ and acceptor V_{Zn} from 4.8×10^{-11} to $\sim 10 \text{ cm}^{-3}$ [Fig. 4(b)]. Further increase of U_G to about -1.5 eV can increase the acceptor V_{Zn} to $\sim 10^6 \text{ cm}^{-3}$ and reduce the Fermi level to 0.97 eV, a weak p -type doping region. Because V_{Zn} possesses the lowest acceptor level at 0.97 eV among all the defects here [Fig. 3(a)], we reach the p -type doping limit for the MBE. Note that the terraces of Fermi level around 1.85 and 0.97 eV [Fig. 4(a)]

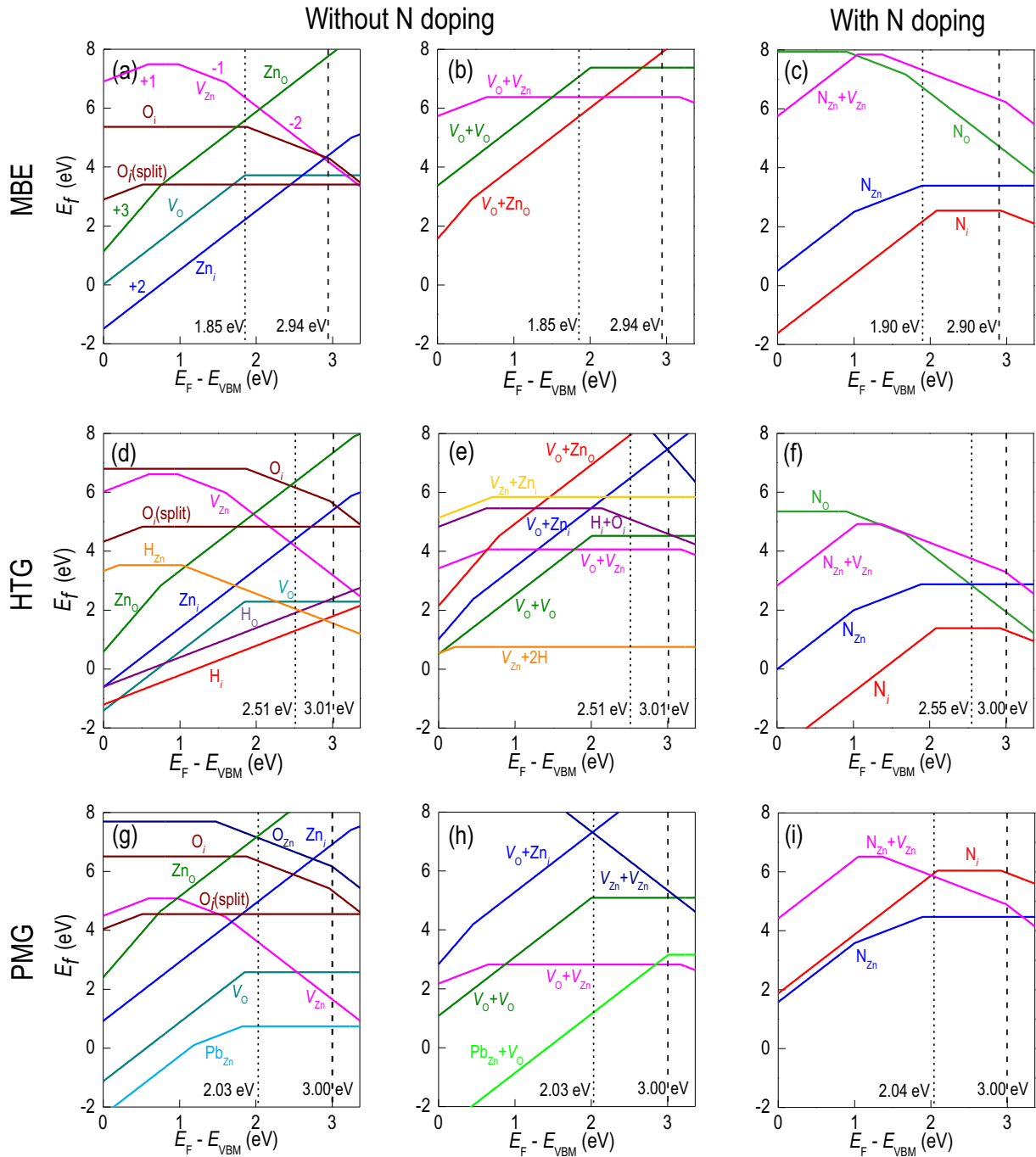


FIG. 3. Defect-formation energy in ZnO for the (a)–(c) MBE, (d)–(f) HTG, and (g)–(i) PMG environment without external voltage. Point defects, pair defects, and nitrogen-dopant defects are shown in (a), (d), (g); (b), (e), (h); and (c), (f), (i), respectively, for easy visualization. Vertically dotted lines in (a), (b), (d), (e), (g), (h) and (c), (f), (i) indicate self-consistent Fermi levels at growth temperatures without and with nitrogen doping, respectively, while vertically dashed lines indicate those reequilibrating at an after-growth temperature of 300 K.

are caused by the neutral charge state of O_i and V_{Zn} below 1.85 and 0.97 eV [Fig. 3(a)], respectively.

For the HTG, a U_G of about -1.4 eV is capable to shift Fermi level to the p -type doping region at 0.97 eV [Fig. 4(c)]. Meanwhile, the dominant donor H_i^+ is dramatically reduced from 3.2×10^{12} to 4.5×10^9 cm^{-3} , and the dominant acceptor H_{Zn}^- is increased from 7.1×10^6 to 4.8×10^9 cm^{-3} [Fig. 4(d)]. Because the lowest acceptor level of H_{Zn} is at 1.04 eV [Fig. 3(d)], close to that of V_{Zn} , no further noticeable re-

duction of Fermi level can be achieved for this growth method. As for the PMG, a U_G of about -0.5 eV decreases Fermi level to 1.84 eV [Fig. 4(e)], followed by three jumps to 0.97 eV. The dominant donor $(Pb_{Zn} + V_o)^{2+}$ is reduced from 2.8×10^{16} to 6.4×10^{12} cm^{-3} , and the dominant acceptor V_{Zn} is increased from 2.8×10^{14} to 1.2×10^{18} cm^{-3} [Fig. 4(f)]. These results show that a proper positive band bending can efficiently decrease the spontaneous n -type defects in ZnO for all the three growth methods and meanwhile increase the p -type defects,

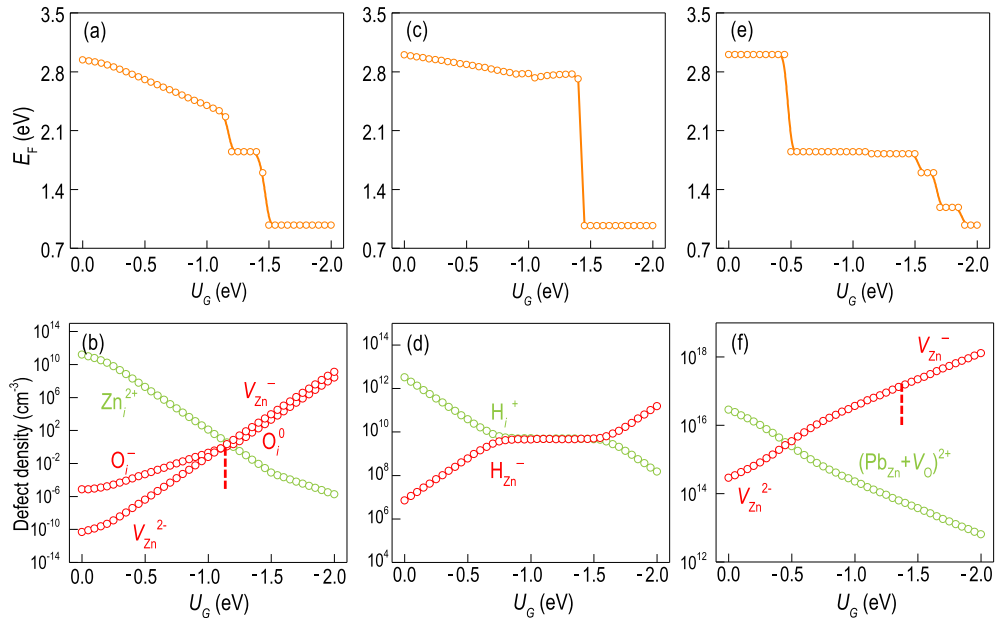


FIG. 4. Dependence of self-consistent Fermi level and dominant n - and p -type defects with band bending U_G for ZnO grown by (a), (b) MBE, (c), (d) HTG, and (e), (f) PMG. Vertical red dashed lines in (b) and (f) indicate positions where defect charge states change. After-growth temperature T_{AG} is set to 300 K.

leading to an ultimate limit of Fermi level at ~ 0.97 eV set by the lowest acceptor level of V_{Zn} or H_{Zn} .

To reveal the ultimate p -type doping limit of ZnO for the previously studied external dopants, we compare the defect-energy levels (thermodynamic transition levels) of four p -type dopants for ZnO [43–46]: nitrogen, arsenic, phosphorus, and silver. Figure 5 shows that among all the 13 defects, N_O possesses the lowest acceptor level at 0.90 eV, which is slightly lower than that of V_{Zn} at 0.97 eV. Therefore, none of these dopants can push the Fermi level of ZnO below 0.90 eV. To achieve a more efficient p -type doping, we envision the need to identify alternative dopants with even lower acceptor-energy levels and employ the voltage-assisted doping method to enable an effective control over the defect concentrations.

D. Experimental realization of the proposed approach

We finally propose a schematic device to realize the voltage-assisted doping method based on the edge-defined

film-fed growth method [47]. As shown in Fig. 6(a), an external voltage can be applied between the top and bottom electrodes in contact with crystal. For ZnO, a positive voltage is applied to the bottom electrode, where excess electrons accumulate and induce a downward band bending that promotes the negatively charged defects but depresses the positively charged defects. Although the band bending could be small at the beginning due to the initial n -type doping in the seed crystal, the external voltage can lead to a reduced n -type doping and subsequently a stronger band bending. When the growth continues and the crystal is pulled up, the band bending increases and the Fermi level decreases further [Fig. 6(b)]. Because the growth front is kept around the bottom electrode, a homogeneous doping should be achieved, irrespective of the gradient of band bending in Fig. 2(a). One final note is that the temperature gradient and growth speed should be controlled in a way that the defect diffusion is significantly lower than the growth speed times a critical length, namely, $D \ll v_z * l$, where D is defect diffusivity, v_z is the out-of-plane growth

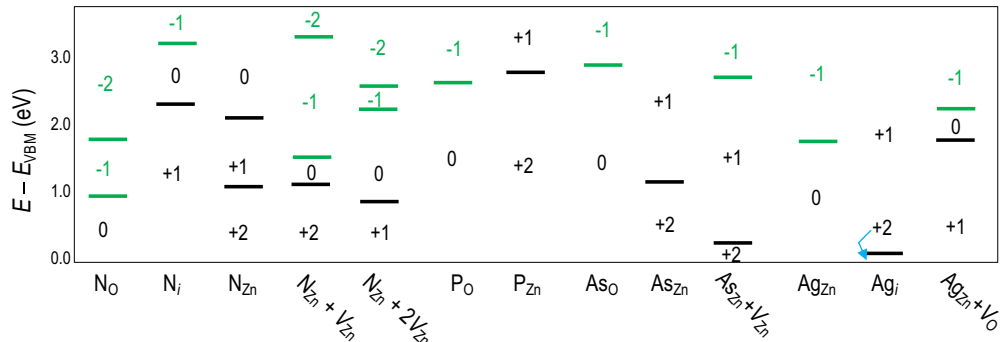


FIG. 5. Thermodynamic transition levels of nitrogen-, arsenic-, phosphorus-, and silver-related defects in ZnO.

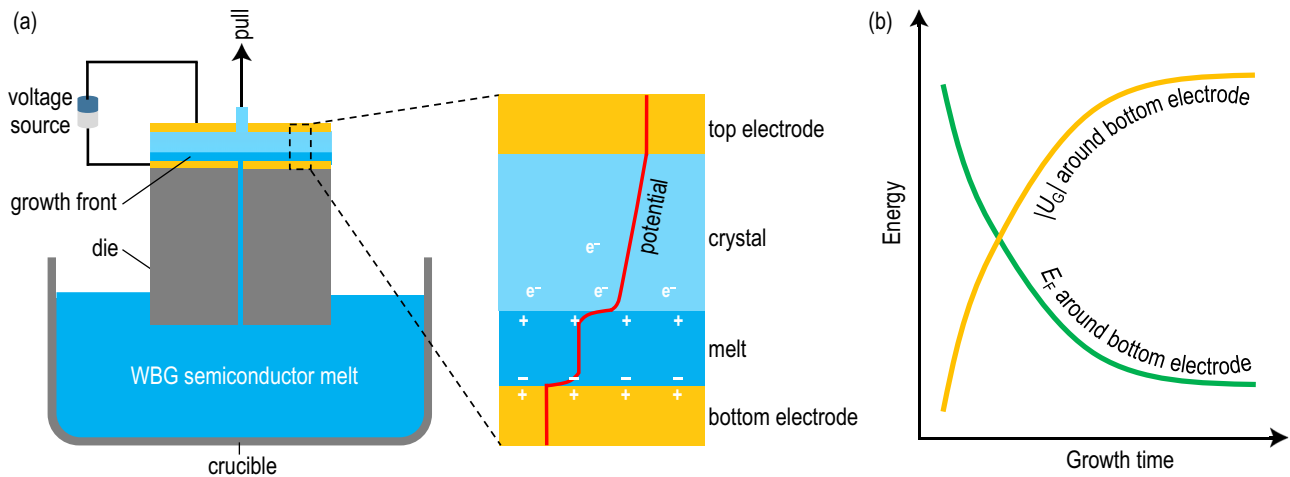


FIG. 6. (a) Proposed device to realize voltage-assisted doping approach and schematic potential distribution across electrodes; (b) schematic change of band bending and Fermi level with growth time for region near positively charged bottom electrode in proposed device.

speed, and l is the length of major band-bending region in which the growth front also locates, so the defects in the region of weak band bending are largely frozen.

IV. CONCLUSION

In summary, we propose a voltage-assisted doping approach to address the doping asymmetry in semiconductors by tuning the band edges and defect thermodynamics using external voltage. We demonstrate the capability of this method in ZnO based on density-functional theory calculations. Our results show that the dominant spontaneous n -type defects in ZnO vary among the MBE, HTG, and PMG, but the voltage-assisted doping approach can dramatically reduce all these donors, increase the acceptors, and successfully bring the Fermi level to the p -type doping limits set by the lowest acceptor levels. Because the proposed approach is based on the

fundamental defect thermodynamics, it should be applicable to the doping of semiconductors in general.

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