Supporting information for

Electronic structures of $Zn_{1-x}Ga_xO_{1-x}N_x$ and band offsets of ZnO/$Zn_{1-x}Ga_xO_{1-x}N_x$ heterojunction across the entire concentration range from first principles

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1. Atomic sphere approximation (ASA)

Atomic sphere approximation (ASA) assumes that unit-cell (or supercell) is filled with slightly overlapped atomic spheres to meet the condition of that the total volume of atom spheres equals to the volume of the cell. If the atomic structure is far from close packed, the space between atoms must be filled with vacancy spheres. Different ASA scheme, i.e., different sphere positions and radii, will affect the calculated electronic structure. Wurtzite structure (e.g., ZnO, GaN) can be made nearly close packed by adding two types of vacancy sites. Consider a primitive cell and let the lattice constants of hexagonal wurtzite structure ZnO or GaN: a = 3.2495Å, c/a = 1.60247, u = 0.382c and the unit-cell vectors are $\mathbf{a}_1 = [a, 0, 0]$, $\mathbf{a}_2 = [-1/2a, \sqrt{3}/2a, 0]$, $\mathbf{a}_3 = [0, 0, c]$. The detail positions of atomic spheres are given in Table 1.

To optimize the radii of atomic sphere, we calculated the band structure of pure ZnO and GaN crystal at the level of LDA. By compare with band structure obtained with the Vienna Ab initio Simulation Package (VASP), we can get proper the radii for atoms and vacancy spheres as shown in Table 1. Figure s1 shows the band structures obtained from the VASP and our ASA

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under the frame of LMTO, respectively. The agreement is excellent - suggesting the appropriateness of our ASA scheme.

Table 1 Positions and radii of the atomic spheres and empty spheres for ZnO and GaN

site	Zn/Ga		O/N		Vac1		Vac2	
x	0	$\frac{1}{2}$	0	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0
y	0	$\frac{\sqrt{3}}{6}$	0	$\frac{\sqrt{3}}{6}$	0	$\frac{\sqrt{3}}{6}$	$\frac{\sqrt{3}}{3}$	$\frac{\sqrt{3}}{3}$
z	0	$\frac{1}{2}c$	$u \cdot c$	$(\frac{1}{2}+u) \cdot c$	$\frac{1+u}{2} \cdot c$	$\frac{1}{2}u \cdot c$	$\frac{1}{2}u \cdot c$	$\frac{1+u}{2} \cdot c$
Radius(Å)	1.1481		1.1481		0.7654		1.3023	

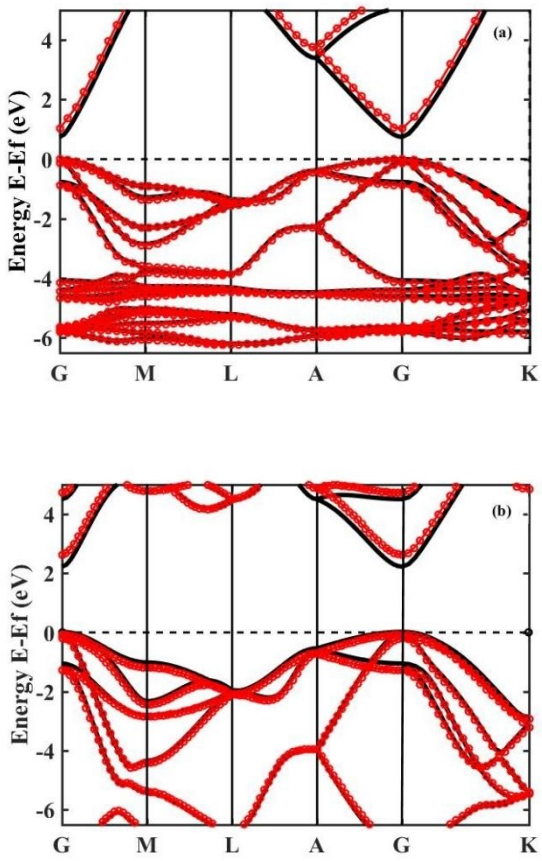

Figure s1. Calculated LDA band structure of (a) pure ZnO and (b) pure GaN. Black solid lines were obtained by the plane wave electronic package VASP, and red circles by NANODSIM

2. Method for calculating the band offsets of heterojunction

We consider a heterojunction A/B which formed by two lattice matched semiconductor A and B. In an individual calculation for each semiconductor A or B, the valence band edge E_v(A) or

E_v(B) can be obtained with respect to the average of the electrostatic potential E_{es}(A) or E_{es}(B) in each bulk material. However, because the calculations on the two materials A and B are carried out independently, namely, the energies in A or B are not respect to the same reference point, the energy relation between the two calculations are ill defined. Therefore, the manipulation of adding or subtracting energies between A and B is of no any physical meaning.

To calculate the band offset of heterojunction A/B, we further carried out a calculation on the heterojunction A/B where each part A and B are long enough so that the electrostatic potential E_{es}(A)' or E_{es}(B)' in the each center regions of A and B are not affected by the interface and can be treated as a bulk. Because the energies in A or B are respect to the same reference point in the calculation on a heterojunction A/B, we can obtain the valence band offset (VBO) from the difference between the valence band edge E_v(A)' and E_v(B)' inside the heterojunction. To calculate the VBO as defined by (E_v(A)'−E_v(B)'), we start from the following relationship,

$$E_v(A)-E_{es}(A) = E_v(A)'-E_{es}(A)', \quad (1)$$

$$E_v(B)-E_{es}(B) = E_v(B)'-E_{es}(B)'. \quad (2)$$

The physical meaning of the above equations is that the difference between the energy edge and the average electrostatic potential of a bulk material keep unchanged. We can easily obtained from Eq. (1) and (2) as following

$$E_v(A)'-E_v(B)' = [E_v(A)-E_{es}(A)]-[E_v(B)-E_{es}(B)]+[E_{es}(A)'-E_{es}(B)']. \quad (3)$$

The items in the first and second square brackets correspond to the energy difference (ΔE_v =[E_v(A)−E_{es}(A)]−[E_v(B)−E_{es}(B)]) between the valence band edges of the two independent bulk semiconductors A and B that form the heterojunction, and the items in the third square brackets the lineup of the potential through the heterojunction (ΔV =[E_{es}(A)'−E_{es}(B)']), respectively.

For conduction band offset, the same calculation procedure can be applied. Clearly, the band offset can be calculated by

$$VBO\ (CBO) = \Delta E_{v(c)} + \Delta V\ . \quad (4)$$

3. Table 2: Band gaps of $Zn_{1-x}Ga_xO_{1-x}N_x$ vs the concentration of GaN *x*. The energy unit is eV.

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
E_g	3.369	1.846	1.585	1.485	1.485	1.524	1.644	1.826	2.086	2.528	3.468

4. Table 3: ΔE_v, ΔE_c , ΔV, VBO and CBO of $ZnO/Zn_{1-x}Ga_xO_{1-x}N_x$ heterojunctions vs the concentration of GaN *x,* The energy unit is eV.

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
ΔE_v	0	-0.907	-1.0183431	-1.0447376	-1.0729009	-1.1137174	-1.1308605	-1.1241871	-1.119888	-1.0192073	-0.7629046
ΔE_c	0	0.616	0.7656569	0.8394624	0.8112991	0.7313826	0.5940395	0.4194129	0.163012	-0.1780073	-0.6641046
ΔV	0	-0.163266	-0.2803	-0.3564641	-0.3945595	-0.4054439	-0.3863962	-0.3455797	-0.2829944	-0.2040825	-0.1061229
VBO	0	-1.188	-1.3748072	-1.4392971	-1.4783448	-1.5001136	-1.4764402	-1.4425558	-1.364787	-1.2232898	-0.7702275
CBO	0	0.336	0.4091928	0.4449029	0.4058552	0.3449864	0.2484598	0.1010442	-0.081887	-0.3820898	-0.8690275