Supplementary Information for Segregation tendencies of transition-metal dopants in wide band gap semiconductor nanowires

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Figure S1 summarizes the computational procedure to obtain the extrapolated energy differences in the dilute defect limit.

Figures S2 and S3 summarize the calibration of the U values for the $3d$ states of the host metal atoms and transition-metal impurities, respectively.

Figure S4 displays the plots of formation energies (segregation energy and barrier heights) with respect to the distance between the dopant and the nanowire center (the Fermi level) for substitutional Bi defects in Bi-doped ZnO nanowire.

Table S1 lists the spin-up and spin-down band gaps for undoped, doped and adatom adsorbed nanowires.

Figure S5 shows the k-dependent spin splitting energy of the lowest conduction band for Mn-doped GaN and Co-doped ZnO nanowires.

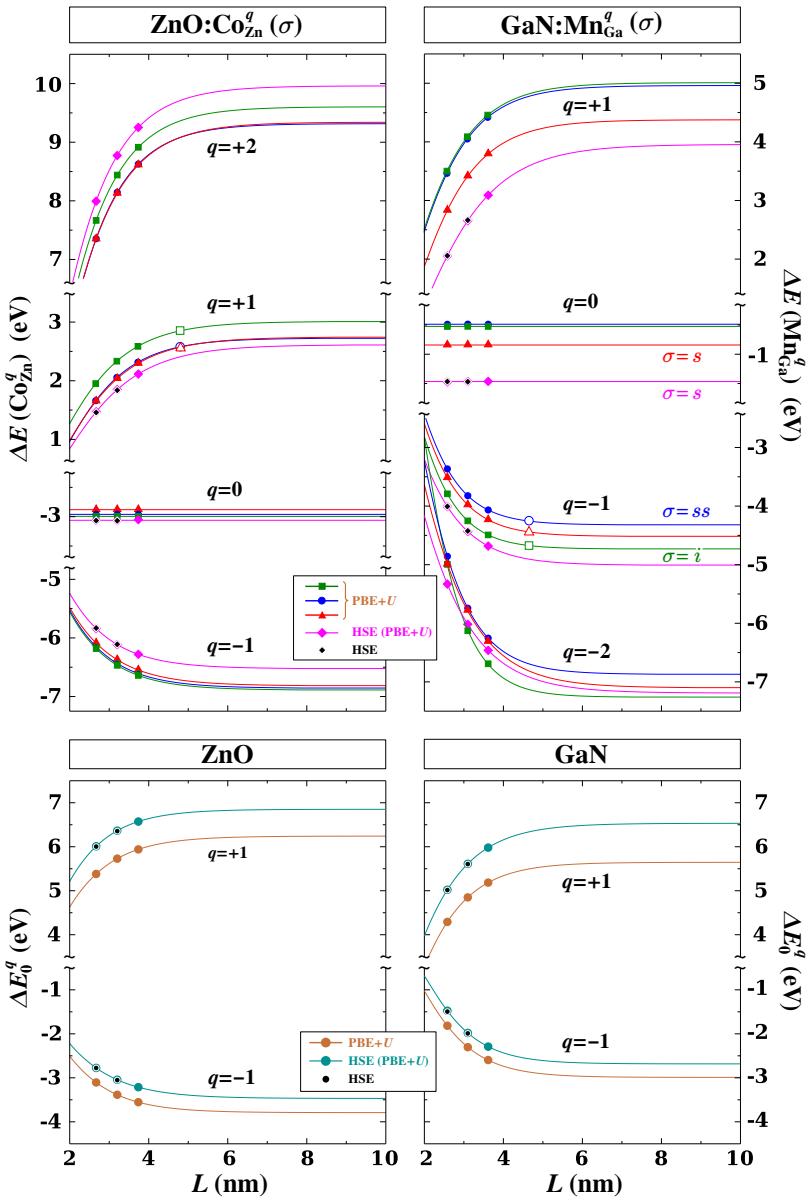

Fig. S1. The procedure to obtain the extrapolated energy differences in the dilute defect limit is based on studying the variation of the energy differences $\Delta E(\mathrm{B}^q_\mathrm{A}(\sigma)) = E(\mathrm{B}^q_\mathrm{A}(\sigma)) - E_0$ and $\Delta E^q_0 = E^q_0 - E_0$ with the supercell length L obtained from density-functional supercell calculations, as illustrated here. The symbols represent the result of PBE+U, non-self-consistent HSE(PBE+U) and fully self-consistent HSE calculations performed for a set of values of $L = nc$ with $n = 5, 6, 7$ and 9, where c denotes the length of periodicity along the wire axis. E_0 and $E(\mathrm{B}^q_\mathrm{A}(\sigma))$ denote the total energy of the supercells containing the defect-free nanowire and the nanowire with defect $\mathrm{B}^q_\mathrm{A}(\sigma)$, respectively; E^q_0 denotes the total energy of the supercell with a net charge q, containing the defect-free nanowire alone. The extrapolated values of these energy differences in the dilute defect limit corresponding to $L \to \infty$ are obtained from fitting in the form $\Delta E = \Delta E_\infty \left(1 + Ce^{-L/l}\right)^3$, the results of which are represented by the solid curves. The points with the open symbols were not used in fitting.

The following technical points are worth noting:

(i) For $\mathrm{Co}^+_\mathrm{Zn}(\sigma)$ and $\mathrm{Mn}^-_\mathrm{Ga}(\sigma)$ defects, the calculated points for $L = 9c$ (the open symbols) that were not used in fitting fall on the curves that were fitted to the solid symbols, and reach the plateau of the solid curves. This demonstrates the convergence of the results obtained from the extrapolation procedure.

(ii) The difference between the energy differences from non-self-consistent HSE calculations with the PBE+U wave functions (the purple diamonds) and those from fully self-consistent HSE calculations (the black diamonds) is on the order of 10 meV. This shows that the energy differences obtained via extrapolation of non-self-consistent and self-consistent HSE energies would differ insignificantly.

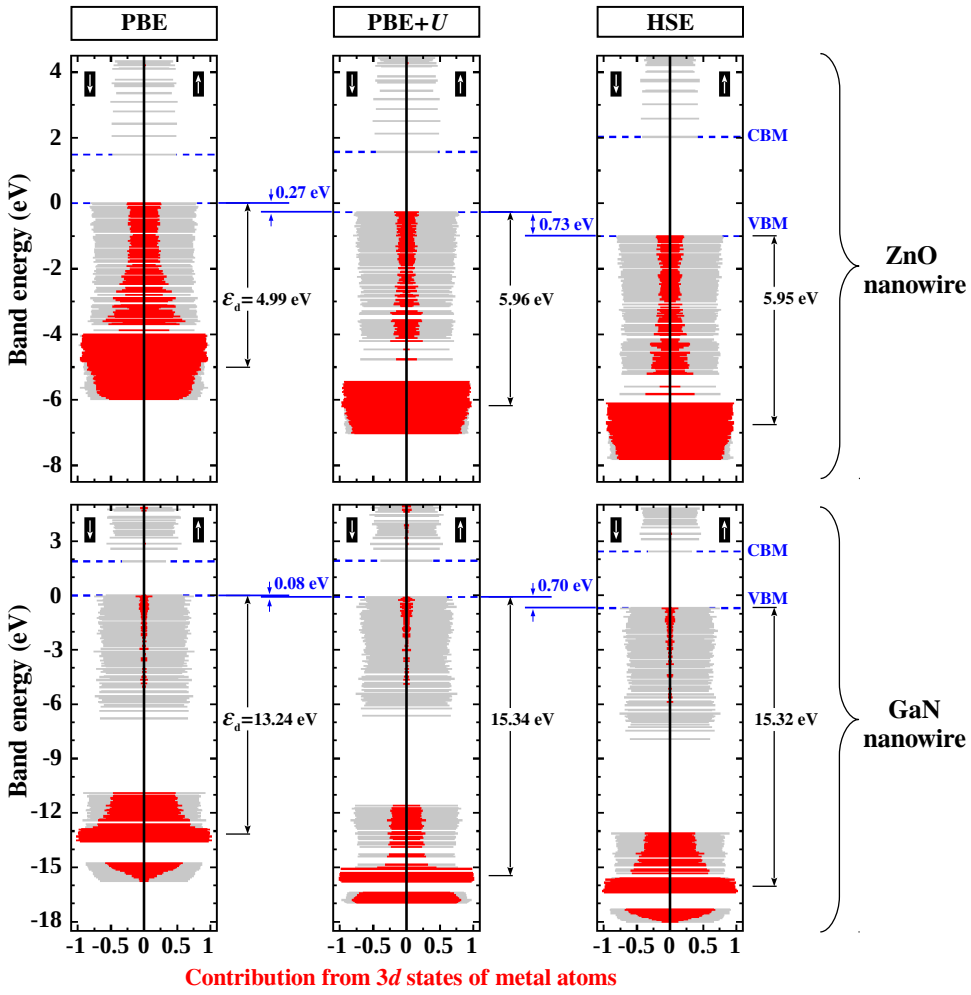

Fig. S2. The contributions from the 3*d* states of metal (Zn or Ga) atoms to the band state wave functions are indicated by the horizontal red line segments. The horizontal gray line segments indicate the total contributions from *all* states of *all* atoms. These contributions were computed by summing up the angular-momentum-resolved contributions from each atom, which were obtained by projecting the state wave functions onto spherical harmonics within a sphere around each atom.

The energy difference indicated by ε_d is used to calibrate the U values. The PBE+U calculations with $U = 3.8$ and 4.8 eV for Zn and Ga, respectively, yield $\varepsilon_d = 5.96$ and 15.34 eV for ZnO and GaN nanowires, respectively, which are nearly the same as the respective HSE-calculated values.

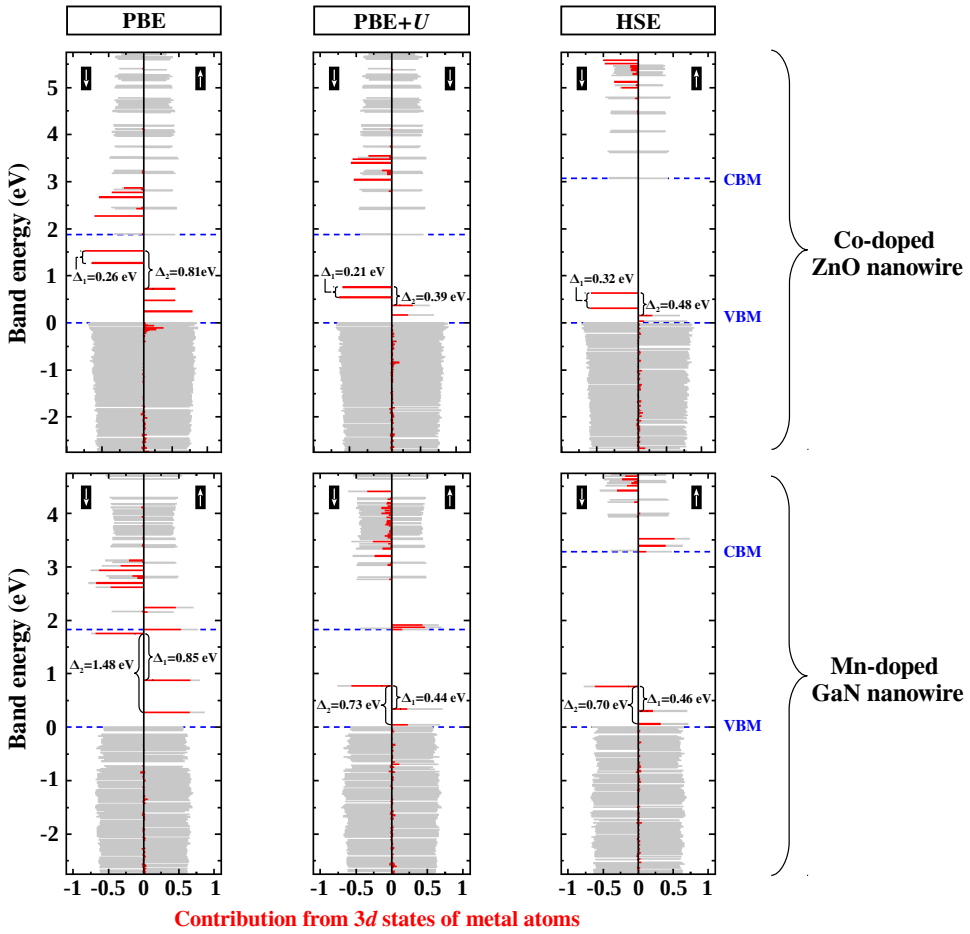

Fig. S3. The contributions from the 3*d* states of dopants (Co or Mn) to the band state wave functions are indicated by the horizontal red line segments. The horizontal gray line segments indicate the total contributions from *all* states of *all* atoms. These contributions were computed by summing up the angular-momentum-resolved contributions from each atom, which were obtained by projecting the state wave functions onto spherical harmonics within a sphere around each atom.

The PBE+U calculations with $U = 2.5$ and 3.6 eV for Co or Mn, respectively, yield the values for exchange splittings of the dopant-induced gap states, indicated by Δ_1 and Δ_2, as closest to the respective HSE-calculated values.

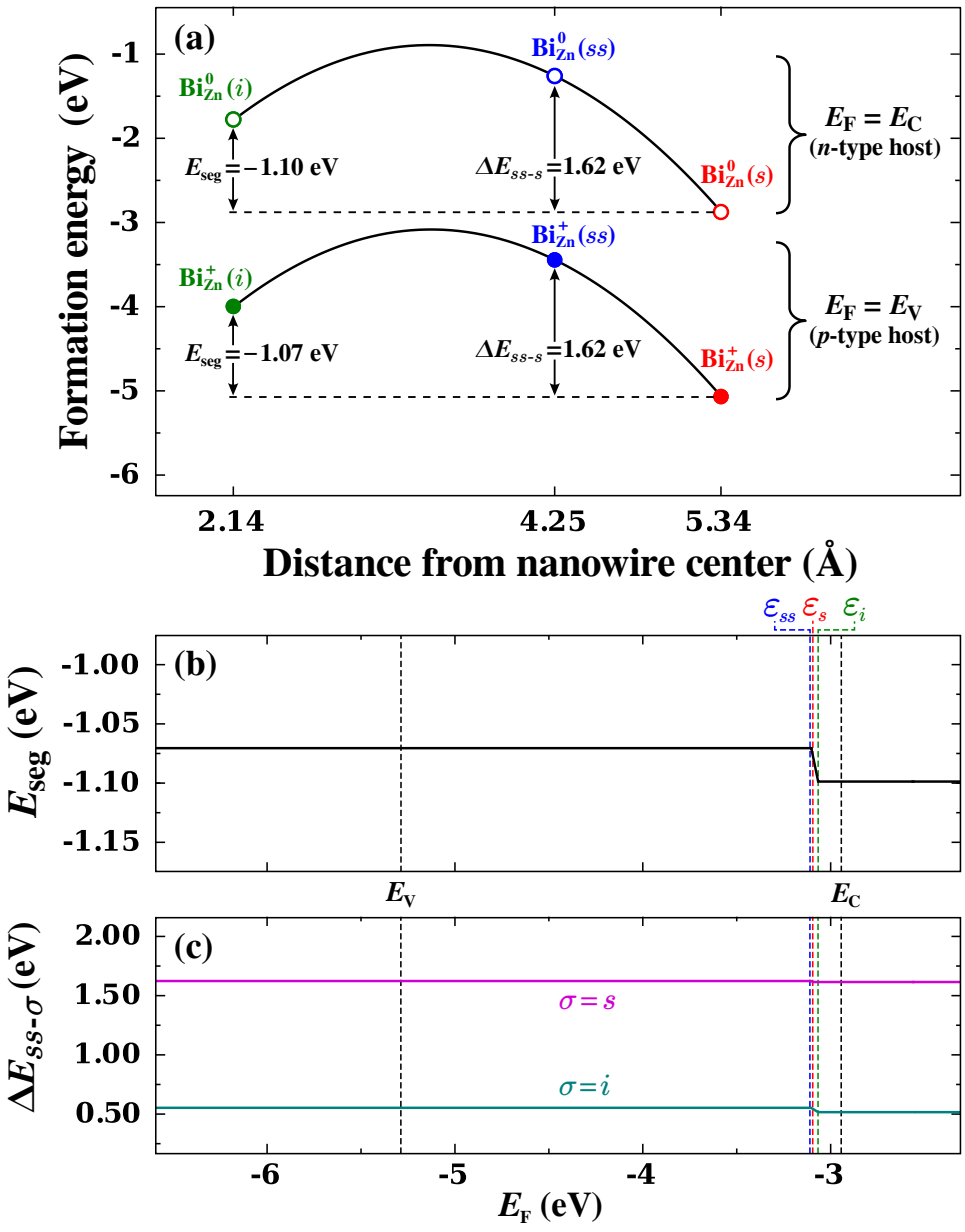

Fig. S4. (a) The formation energies of Bi_{Zn} defects in ZnO:Bi nanowire as a function of the distance between the dopant and the nanowire center. $E_F = E_C$ ($E_F = E_V$) implies that the host nanowire is an n-type (p-type) semiconductor. The solid-line curves are parabolas fitted to the calculated points. The variation of (b) the segregation energy E_{seg} and (c) barrier heights $\Delta E_{ss\text{-}s}$ and $\Delta E_{ss\text{-}i}$ with the Fermi level E_F for Bi_{Zn} in ZnO:Bi nanowire. ε_σ is shorthand for $\varepsilon_\sigma(+/0)$, where σ=i, ss, s.

Table S1. The calculated values of spin-up and spin-down band gaps, $E_g^{\uparrow} = \varepsilon_{\rm CBM}^{\uparrow} - \varepsilon_{\rm VBM}^{\uparrow}$ and $E_g^{\downarrow} = \varepsilon_{\rm CBM}^{\downarrow} - \varepsilon_{\rm VBM}^{\downarrow}$, respectively, for pristine, doped and adatom adsorbed nanowires, where $\varepsilon_{\rm VBM}^{\uparrow}$ and $\varepsilon_{\rm VBM}^{\downarrow}$ ($\varepsilon_{\rm CBM}^{\uparrow}$ and $\varepsilon_{\rm CBM}^{\downarrow}$) are the spin-up and spin-down VBM (CBM) energies of the hosts, respectively.

	$E_g^{\uparrow}$ (eV)	$E_g^{\downarrow}$ (eV)
GaN	2.150	2.150
GaN:$\mathrm{Mn_{Ga}}(i)$	2.170	2.155
GaN:$\mathrm{Mn_{Ga}}(ss)$	2.157	2.149
GaN:$\mathrm{Mn_{Ga}}(s)$	2.164	2.159
GaN+Mn	2.110	2.121
ZnO	1.858	1.858
ZnO:$\mathrm{Co_{Zn}}(i)$	1.876	1.869
ZnO:$\mathrm{Co_{Zn}}(ss)$	1.885	1.869
ZnO:$\mathrm{Co_{Zn}}(s)$	1.875	1.866
ZnO+Co	1.736	1.793

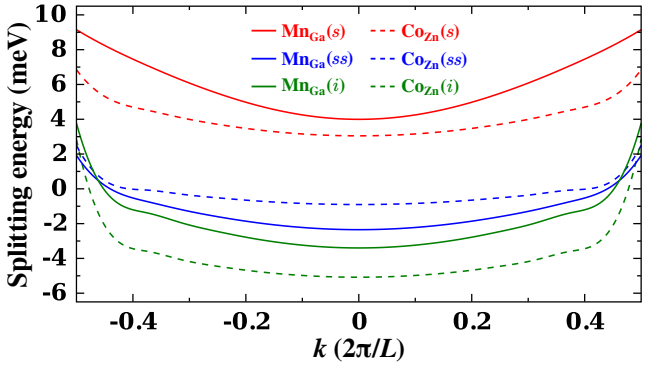

Fig. S5. The k-dependent spin splitting energy of the lowest conduction band for Mn-doped GaN and Co-doped ZnO nanowires.