Electronic Supplementary Material (ESI) for Nanoscale Advances.

ELECTRONIC SUPPLEMENTARY INFORMATION

Modulating the growth of chemically deposited ZnO nanowires and the formation of nitrogen- and hydrogen-related defects using the pH adjustment

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Section S1. Density-Functional Theory Method

The formation energy of defects requires examining the modification of the chemical potentials of species upon introducing a vacancy or impurity atoms in the simulation supercell. In pure bulk ZnO, the chemical potentials should satisfy the following relations [1]:

$$\mu_{ZnO}^{s} = \mu_{Zn} + \mu_{O}$$

$$\Delta H_{ZnO}^{f} = \mu_{ZnO}^{s} - \mu_{Zn}^{s} - \mu_{O_2}^{g}$$

where $\left(\Delta H_{ZnO}^{f}\right)$ is the heat of formation of ZnO, $\left(\mu_{ZnO}^{s}\right)$ is the chemical potential of the bulk ZnO in the wurtzite phase and, $\left(\mu_{Zn}^{s}\right)$ and $\left(\mu_{O_2}^{g}\right)$ are the chemical potentials of the condensed (Zn metal) and of the gaseous (O_2) phases, respectively. Then these expressions can conveniently be re-written as:

$$\mu_{Zn} = \mu_{Zn}^{s} + (1 - \lambda) \times \Delta H_{ZnO}^{f}$$

$$\mu_{O} = \mu_{O_2}^{g} + \lambda \times \Delta H_{ZnO}^{f}$$

Where $\lambda\,(0 \le \lambda \le 1)$ is a parameter defining O-rich $(\lambda = 0)$ or Zn-rich $(\lambda = 1)$ conditions. The chemical potential difference between species is then given by:

$$\Delta\mu = \left(\mu_{Zn} - \mu_{Zn}^{s}\right) - \left(\mu_{O} - \mu_{O_2}^{g}\right) = \left(\mu_{Zn} - \mu_{O}\right) - \left(\mu_{Zn}^{s} - \mu_{O_2}^{g}\right) = (1 - 2\lambda) \times \Delta H_{ZnO}^{f}$$

And should satisfy the obvious condition:

$$\begin{array}{ccc} -\Delta H_{ZnO}^{f} \le & \Delta\mu & \le \Delta H_{ZnO}^{f} \\ (\lambda = 1) & & (\lambda = 0) \\ Zn - rich & & O - rich \end{array}$$

The formation energy of an electrically neutral defect at $T = 0\ K$ is given by [2]:

$$\Omega_D(\mu_{Zn},\mu_O) = E_D - \frac{1}{2}(n_{Zn} + n_O)\mu_{ZnO}^{s} - \frac{1}{2}(n_{Zn} - n_O)\left(\mu_{Zn}^{s} - \mu_{O_2}^{g}\right) - \frac{1}{2}(n_{Zn} - n_O)\Delta\mu$$

Where n_{Zn} and n_O, represent the numbers of Zn and O atoms, respectively. By combining the relations above, one easily obtains:

$$\Omega_D(\mu_{Zn},\mu_O) = E_D - E_{ref}^{total} - n'_{Zn}\mu_{ZnO}^{s} - (n'_{O} - n'_{Zn})\mu_O$$

where, E_{ref}^{total} is the total energy of the reference structure, and n'_{Zn}, n'_{O} are the differences between the numbers of Zn and O atoms in the defected supercells and in the reference structures, respectively. Equally, the formation energy of a defect in a specific charge state (Q) is given by:

$$\Omega_D(\mu_{Zn},\mu_O) = E_D - E_{ref}^{total} - n'_{Zn}\mu_{ZnO}^{s} - \left(n'_{O} - n'_{Zn}\right)\mu_O + Q\left(E_D^{Fermi} + E_{ref}^{VBM}\right)$$

where, E_D^{Fermi} is the Fermi level energy of the defective system with respect to the Valence Band Maximum (VBM), E_{ref}^{VBM}, in the reference system, shifted by the difference between average electrostatic potentials in the defected and the reference systems.

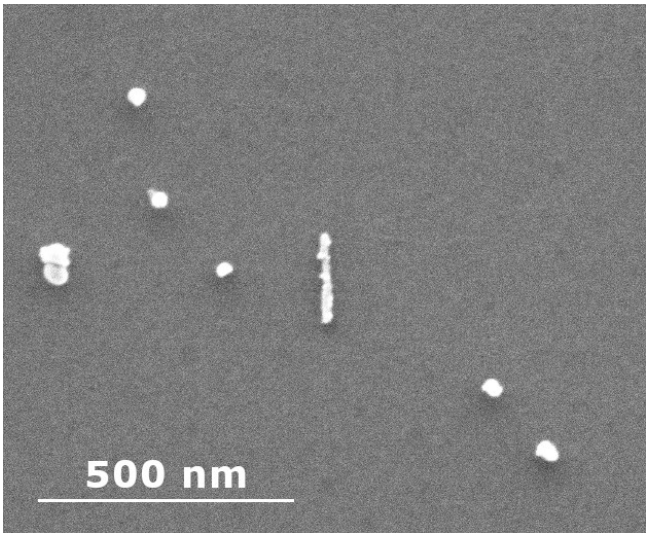

Fig. S2 Top-view field-emission scanning electron microscopy (FESEM) image of the chemical bath deposition (CBD) sample deposited with the pH_0 value of 11.07.

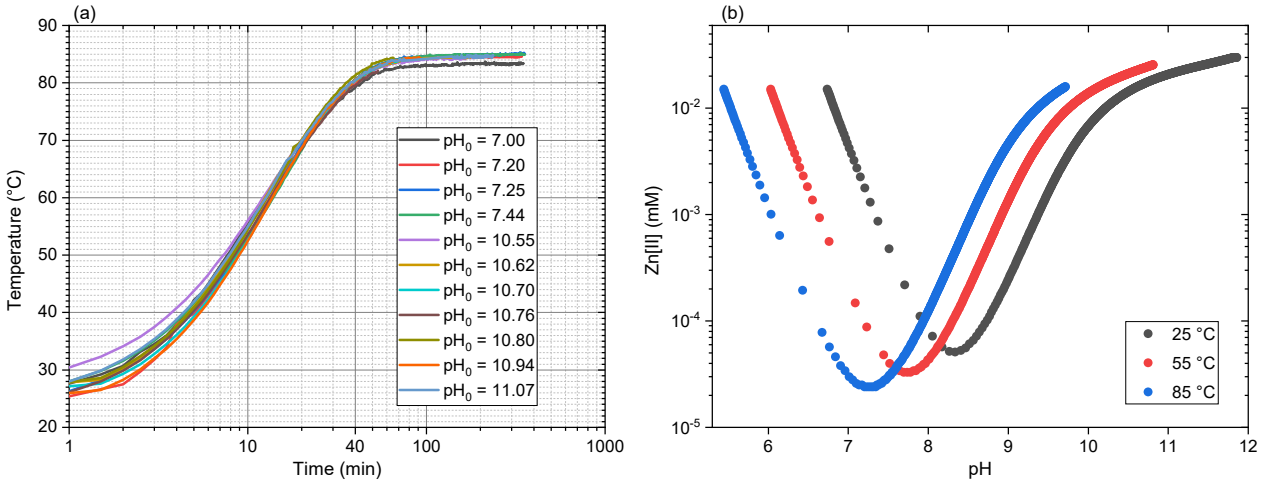

Fig. S3 (a) In situ measurement of temperature during the chemical bath deposition (CBD) of ZnO NWs grown with pH_0 values in the range of 7.00 – 11.07. (b) Theoretical solubility plot of Zn(II) species at different temperatures as a function of the calculated pH, obtained from thermodynamical calculations by Visual MINTEQ.

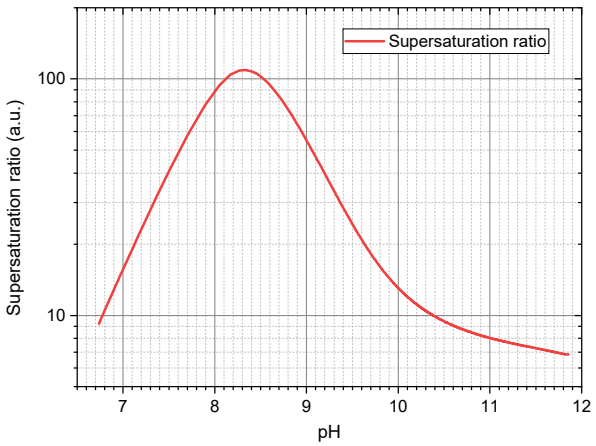

Fig. S4 Theoretical supersaturation ratio of Zn(II) species as a function of the calculated pH, obtained from thermodynamical calculations by Visual MINTEQ.

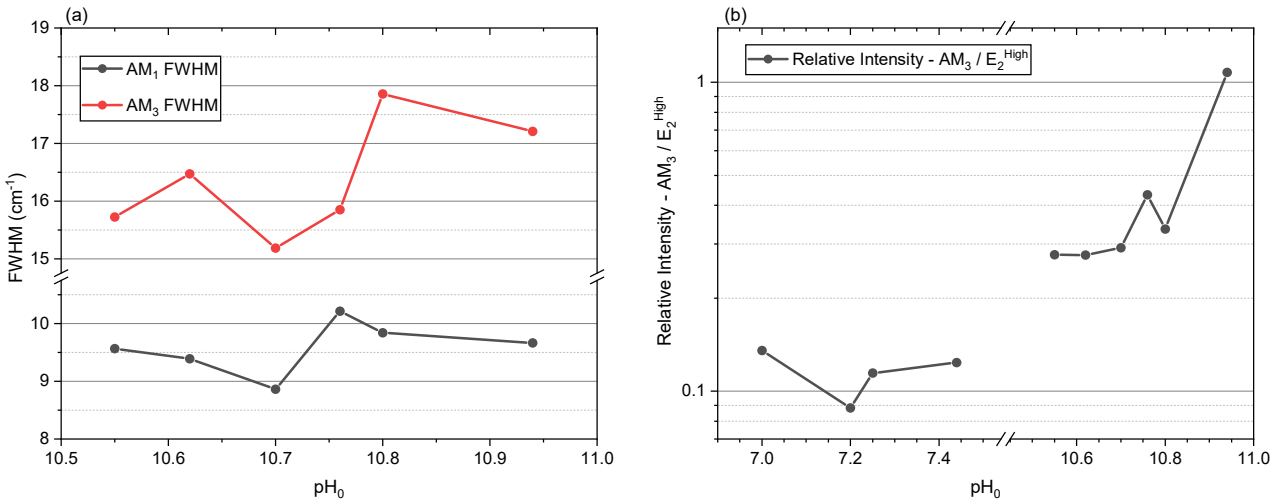

Fig. S5 Evolution of the (a) FWHM of the AM_1 and AM_3 modes, and (b) relative intensity $\left(\frac{AM_3}{E_2{}^{high}}\right)$ for the annealed ZnO NWs series grown by chemical bath deposition (CBD) with pH_0 values in the range of 7.00 – 10.94.

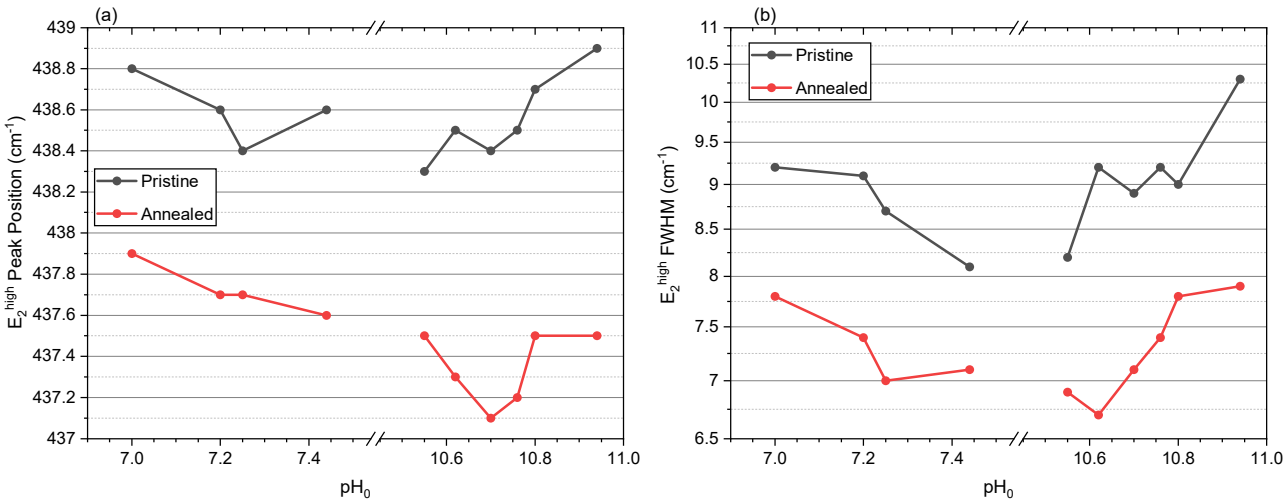

Fig. S6 Evolution of the (a) peak position, and (b) FWHM of the E_2^{high} Raman mode of ZnO NWs grown by chemical bath deposition (CBD) with pH_0 values in the range of 7.00 – 10.94.

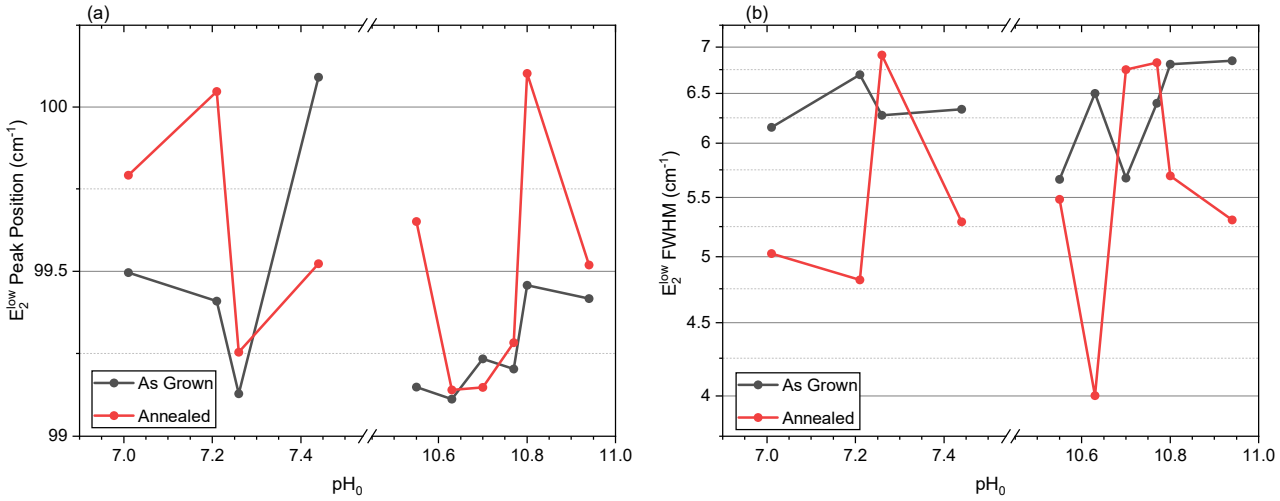

Fig. S7 Evolution of the (a) peak position, and (b) FWHM of the E_2^{low} Raman mode of ZnO NWs grown by chemical bath deposition (CBD) with pH_0 values in the range of 7.00 – 10.94.

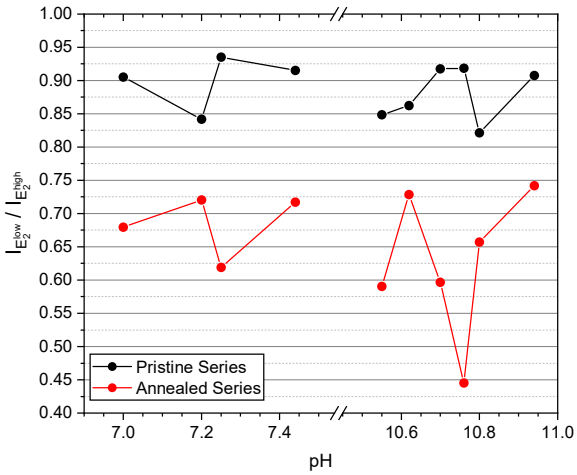

Fig. S8 Intensity ratio of E_2^{low} and E_2^{high} Raman modes of ZnO NWs grown by chemical bath deposition (CBD) with pH_0 values in the range of 7.00 – 10.94.

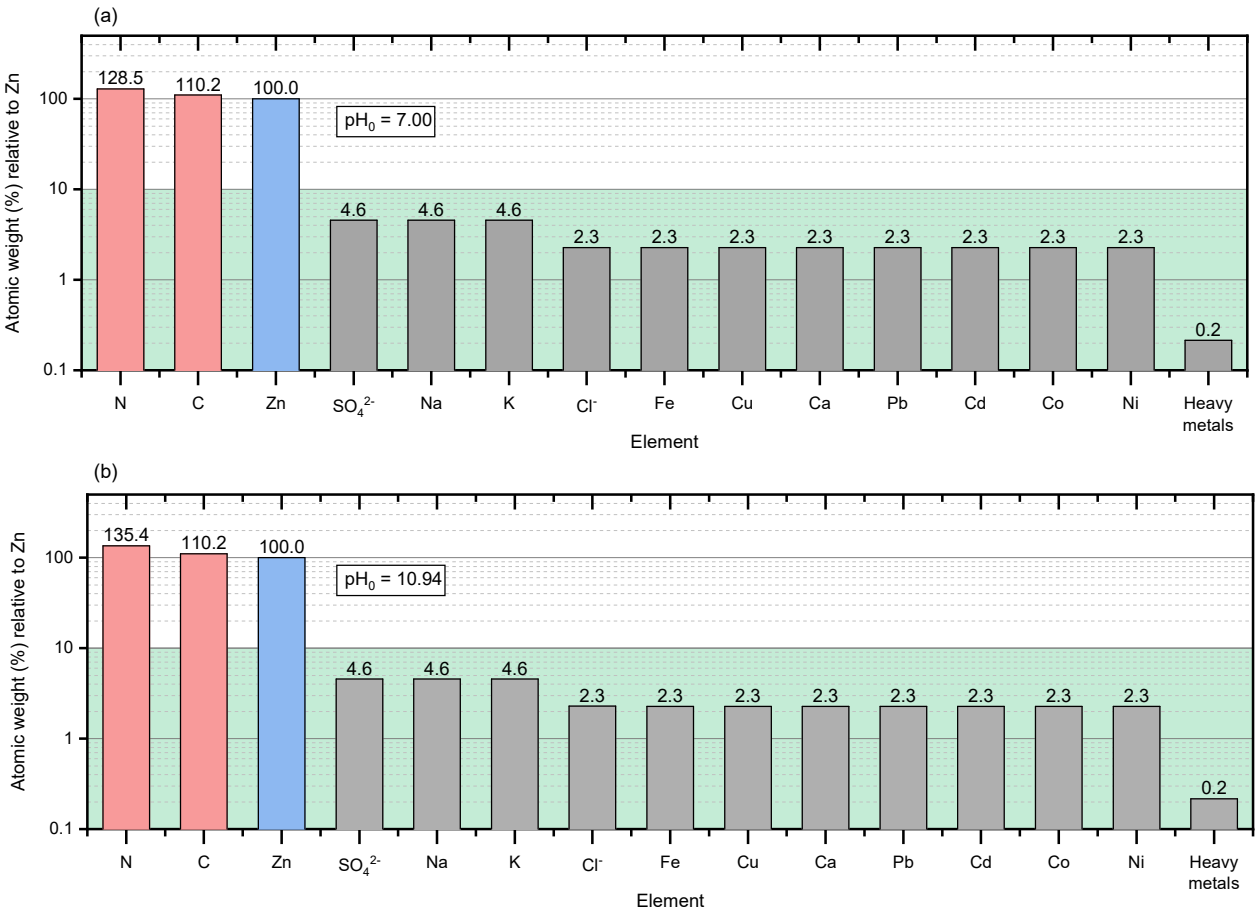

Fig. S9 Atomic weight (%) relative to Zn atoms of the foreign elements present in the chemical bath deposition (CBD) reaction for the growth condition of ZnO NWs at: (a) pH_0 of 7.00 and (b) pH_0 of 10.94. They come from the residual impurities presented in the Certificate of Analysis of the precursors:

$Zn(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich), HMTA – $C_6H_{12}N_4$ (Sigma-Aldrich) and Ammonium hydroxide solution – NH_4OH (Sigma-Aldrich).

References

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2. Qian, G. X., Martin, R. M. & Chadi, D. J. First-principles study of the atomic reconstructions and energies of Ga- and As-stabilized GaAs(100) surfaces. *Phys. Rev. B* **38**, 7649–7663 (1988).