Stabilization of ZnO(0001) Surface and Self-assembled Nanostructures studied by Scanning Probe Microscopy

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SPM investigation

Scanning Tunneling Microscopy (STM) & Scanning Force Microscopy (SFM)

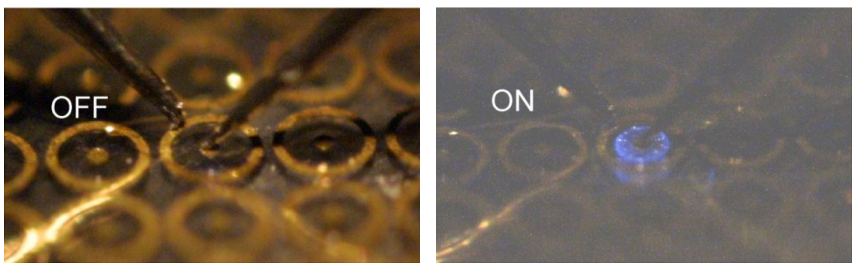
- Topographic images
  - (iii) X-sectonal STM study of ZnO
  - (ii) Nucleation & growth of Co on ZnO
- Electronic properties
  - LDOS
  - Surface potential
  - **(i) Stabilization of ZnO polar surface with charged surface Nano-defects**

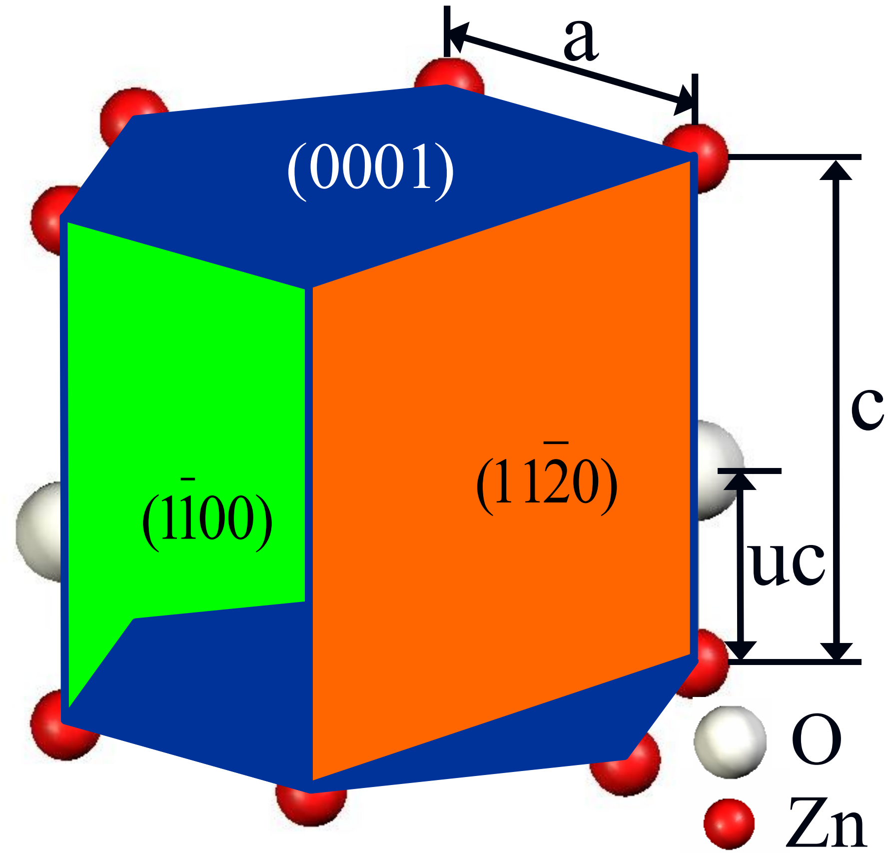
Part I.
Stabilization of ZnO(0001) Polar plane with surface Nano-defects

Wurtzite ZnO

- Direct band-gap of 3.37 eV, near-UV emission, a large excitation binding energy (60 meV), the transparent conductivity and catalysis properties.

Light-emitting diode based on ZnO



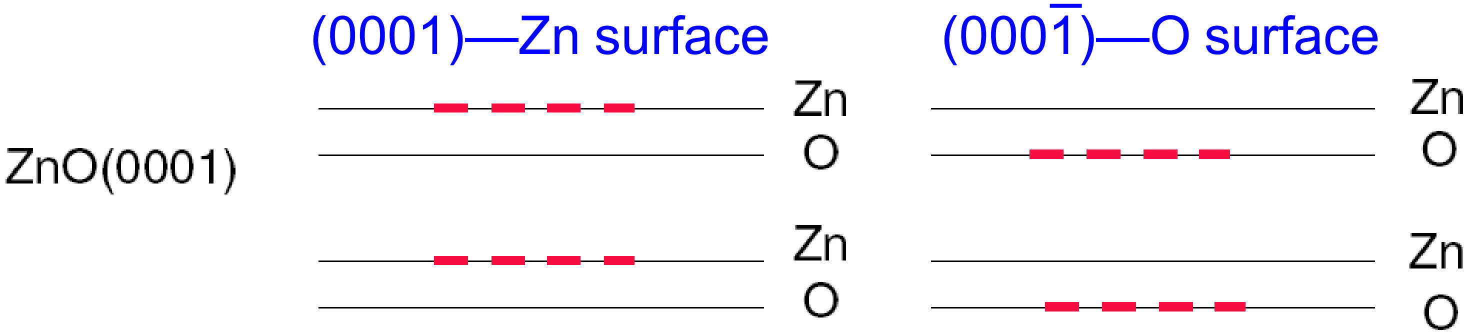


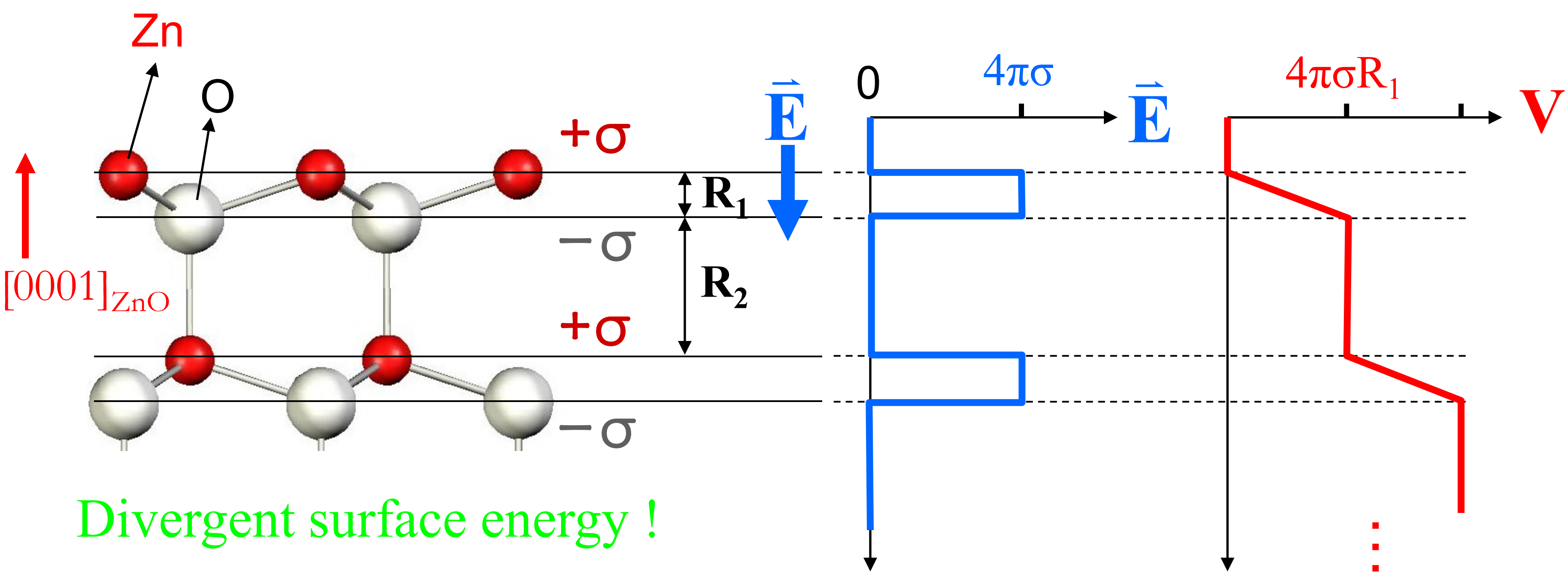
- Wurtzite ZnO is easy to fabricate as crystalline structure along c-axis.

There are polarity problems on the $(0001)_{ZnO}$ surfaces.

	LDA	PBE	Expt.
a(Å)	3.193 (−1.7%)	3.282 (+1.0%)	3.250
c(Å)	5.163 (−0.8%)	5.291 (+1.6%)	5.207
c/a	1.617	1.612	1.602
u	0.3783	0.3792	0.3825

Polar surface of ZnO

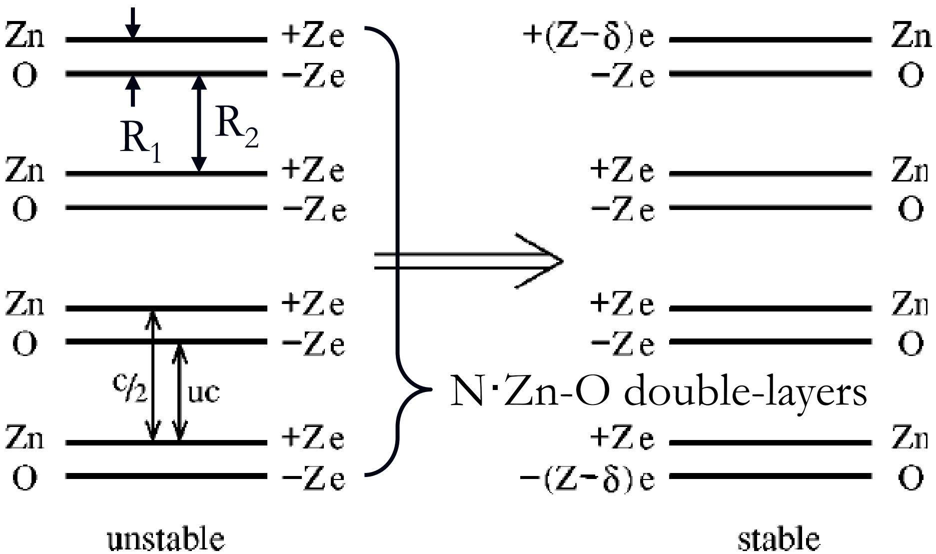




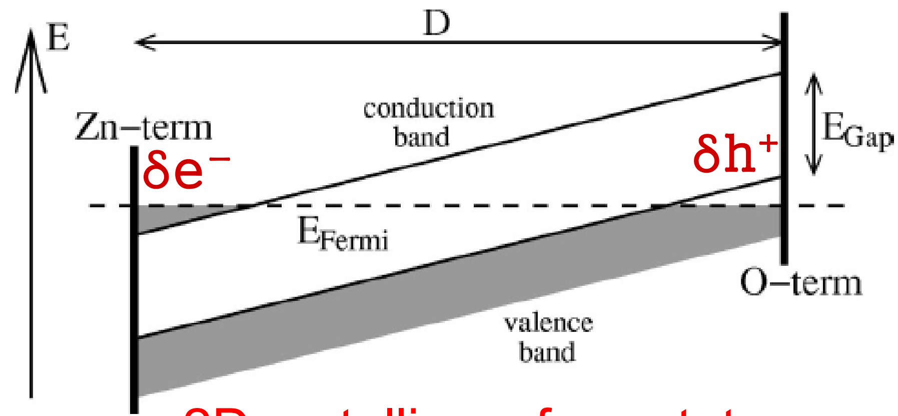
Divergent surface energy !

The (0001)-Zn and (0001)-O polar surfaces need to be stabilized by **quenching the internal electrostatic dipolar field.**

Stabilizing mechanism for polar surface



creating surface state for charge transfer



2D metallic surface state

by PRL (86) 3811 (2001), PRB (67) 035403 (2003), PRB (68) 245409 (2003), PRB(77) 035332 (2008)

$$\mathbf{R}_1 = \left(\frac{\mathbf{c}}{2} - \mathbf{uc}\right) = 0.65\,\mathring{\mathrm{A}},\ \mathbf{R}_2 = \mathbf{uc} = 1.99\,\mathring{\mathrm{A}}$$

$$\mathbf{N} \cdot \mathbf{Ze} \cdot \mathbf{R}_1 = \delta\mathbf{e} \cdot \mathbf{N}(\mathbf{R}_1 + \mathbf{R}_2)$$

$$\Rightarrow \delta = \frac{\mathbf{R}_1}{\mathbf{R}_1 + \mathbf{R}_2} \cdot \mathbf{Z} = (1 - 2\mathbf{u}) \cdot \mathbf{Z} \cong \frac{1}{4} \cdot \mathbf{Z}$$

charge compensation

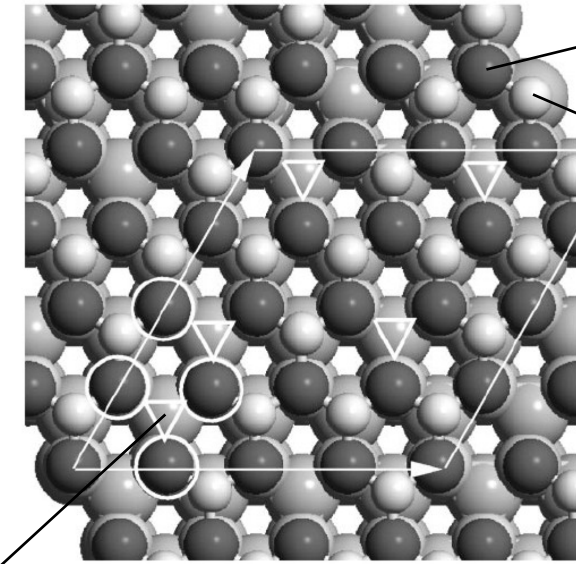
by Tasker, J. Phys. C 12, 4977 (1979)

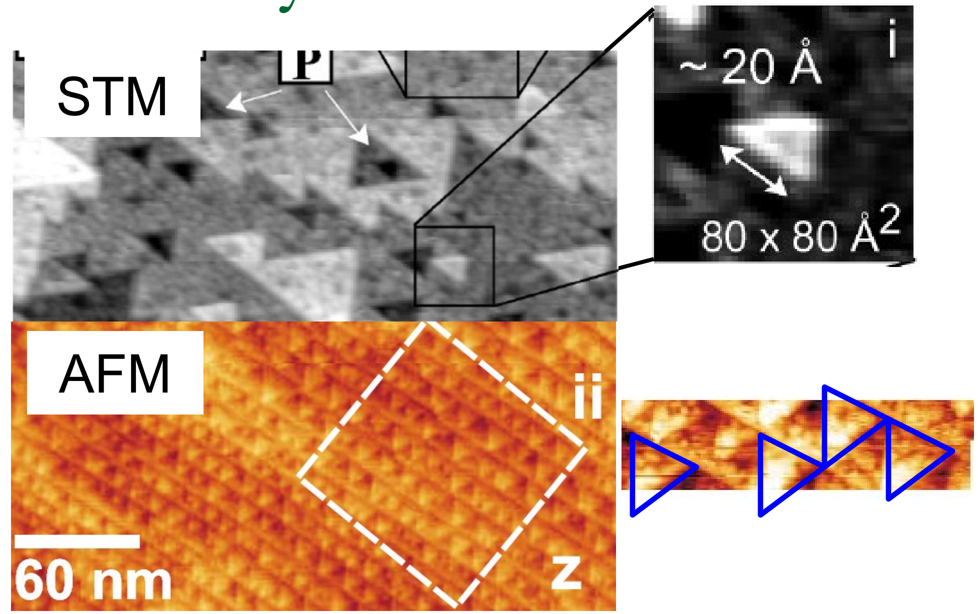
However, the 2D metallic surface state has been not observed on the (0001)-Zn surface by ARPES measurements.

by PRB (78) 155414 (2008), PRB (79) 075314 (2009)

$(0001)_{ZnO}$ polar surfaces are stabilized by other pathways.

Polar surface Stabilization by Zn vacancies





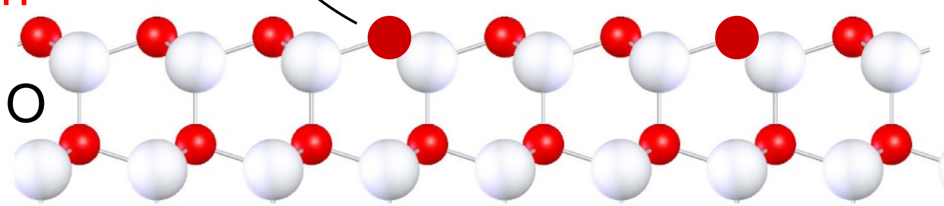
by PRL (90) 016102 (2003), PRB (77) 041405 (2008)

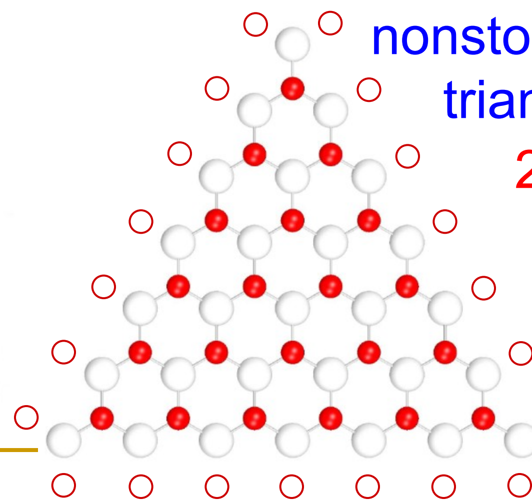
Zn vacancy ➡ compensation charge δ

$$\delta = \frac{\mathbf{R}_1}{\mathbf{R}_1 + \mathbf{R}_2} \cdot \mathbf{Z} \cong \frac{1}{4} \cdot \mathbf{Z}$$

Zn

O





nonstoichiometry ZnO

triangular island

21 Zn : 28 O

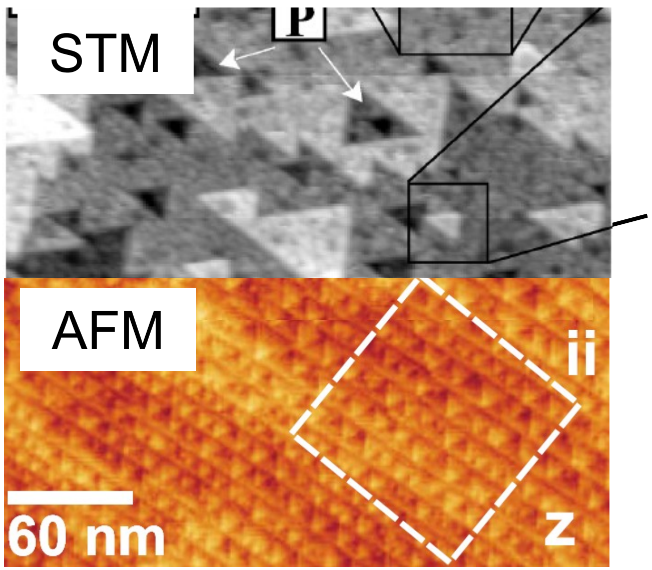
+ 7

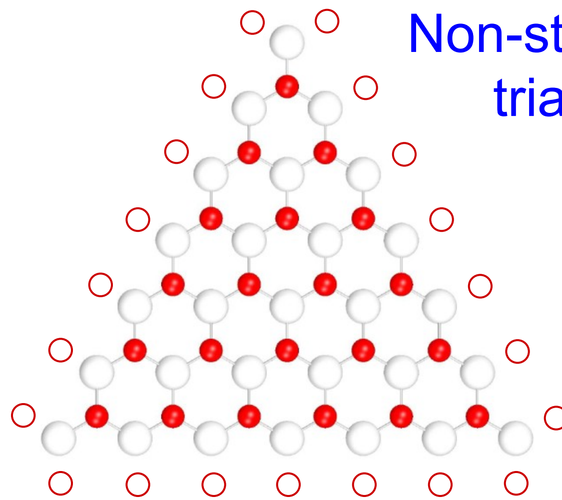
compensation charge δ

by PRB (68) 245409 (2003), PRB (78) 155424 (2008)

Motivation

Evidence of charged surface defects ?





Non-stoichiometry ZnO triangular island

21 Zn : 28 O

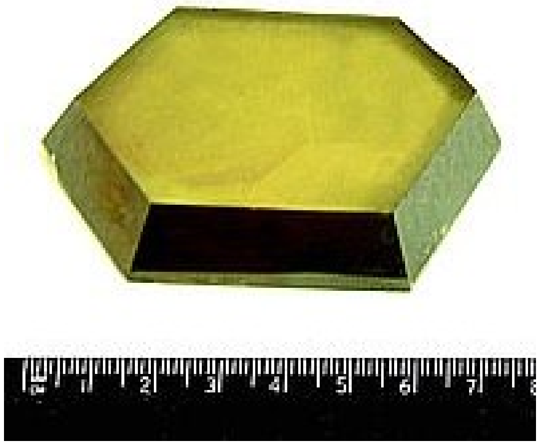
+ 7

Compensation charge δ

Stabilizing mechanism of ZnO polar surface via surface defects?

How to create and control surface defects on ZnO surface?

Experiment



Sample fabrication

The ZnO single crystal was hydrothermally grown in a high pressure autoclaves with 20 – 70 MPa by means of the direct-temperature drop in the aqueous solution of KOH + LiOH at the crystallization temperature of 320 – 400^{o}C. The samples were 7 mm × 2 mm × 0.3 mm slabs as polished by two surfaces of (0001) and (000-1).

Surface cleaning

1. Ion sputtering at 1 keV for 10 min.
2. Annealing at 750^{o}C for 15 min.

The clean Zn-terminated surface can be achieved by 3 - 4 cycles.

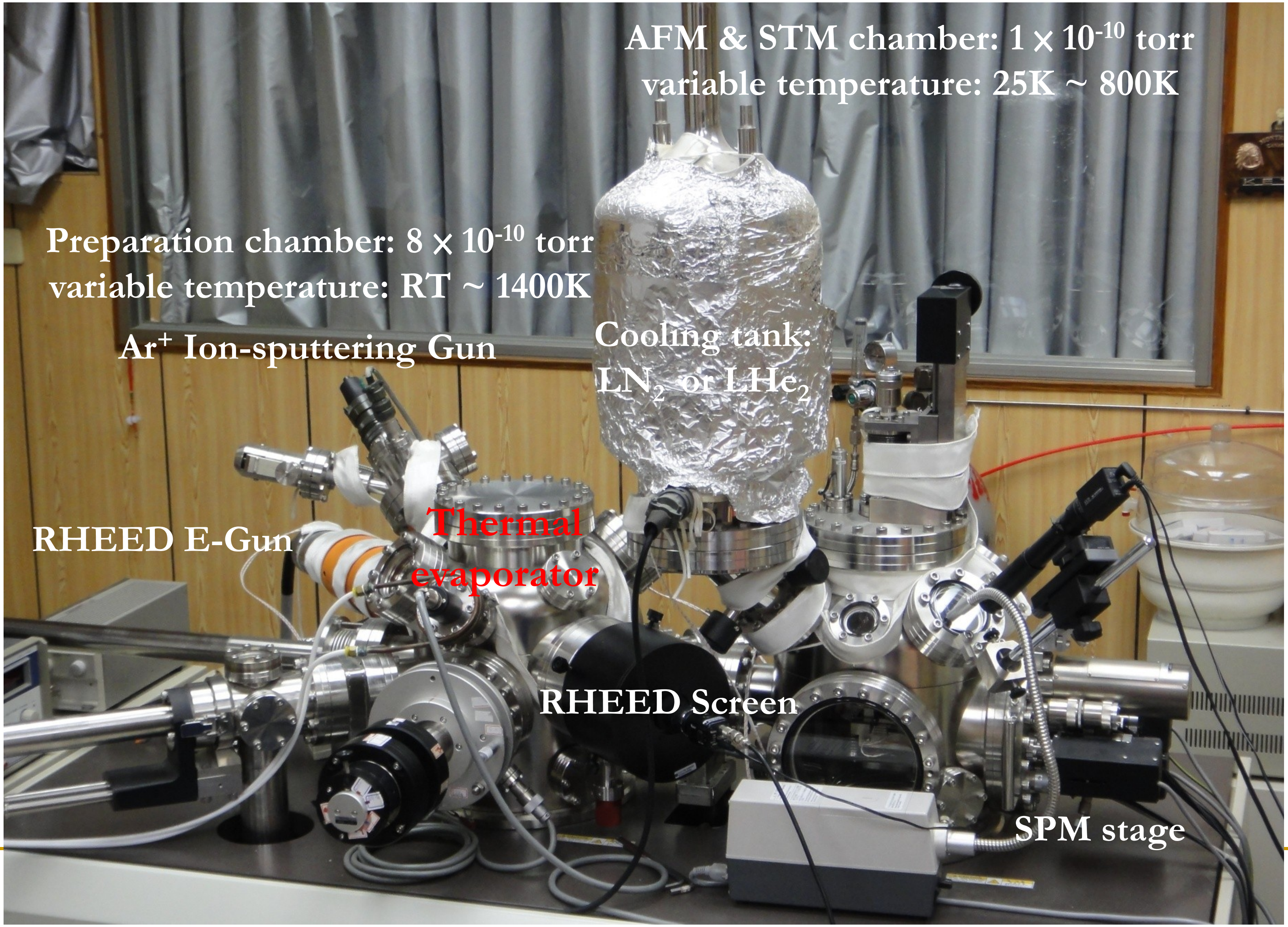
Ion irradiation

After cleaning process, the Zn-(0001) terminated surface was irradiated by Ar^{+} ion beams with E_{ion} at 850^{o}C.

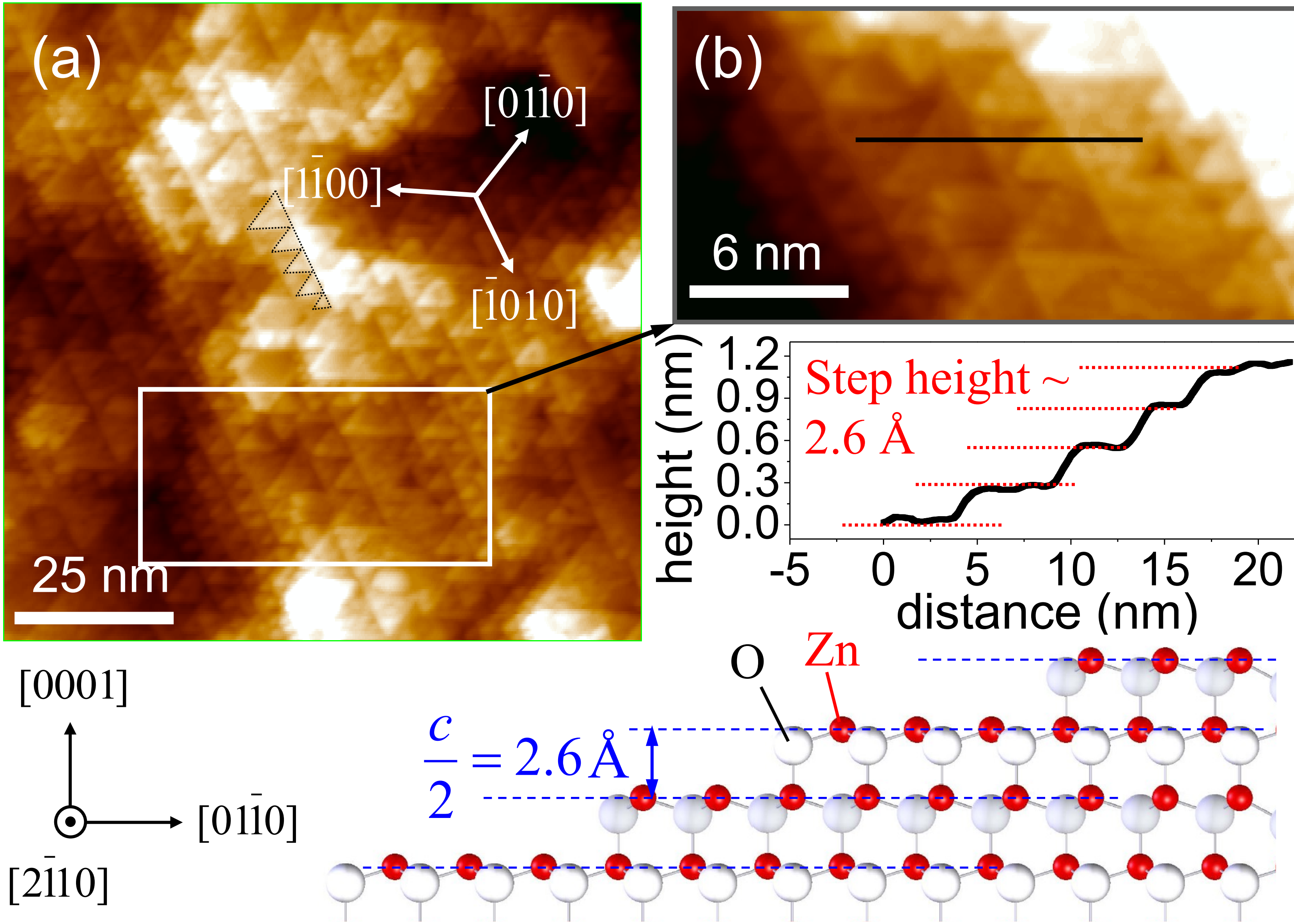
E_{ion}=0.5 - 2.5 keV

The surface structure, morphology and electron properties of samples were *in situ* investigated by **RHEED**, **AFM, SKPM**, **STM** and **STS**, respectively.

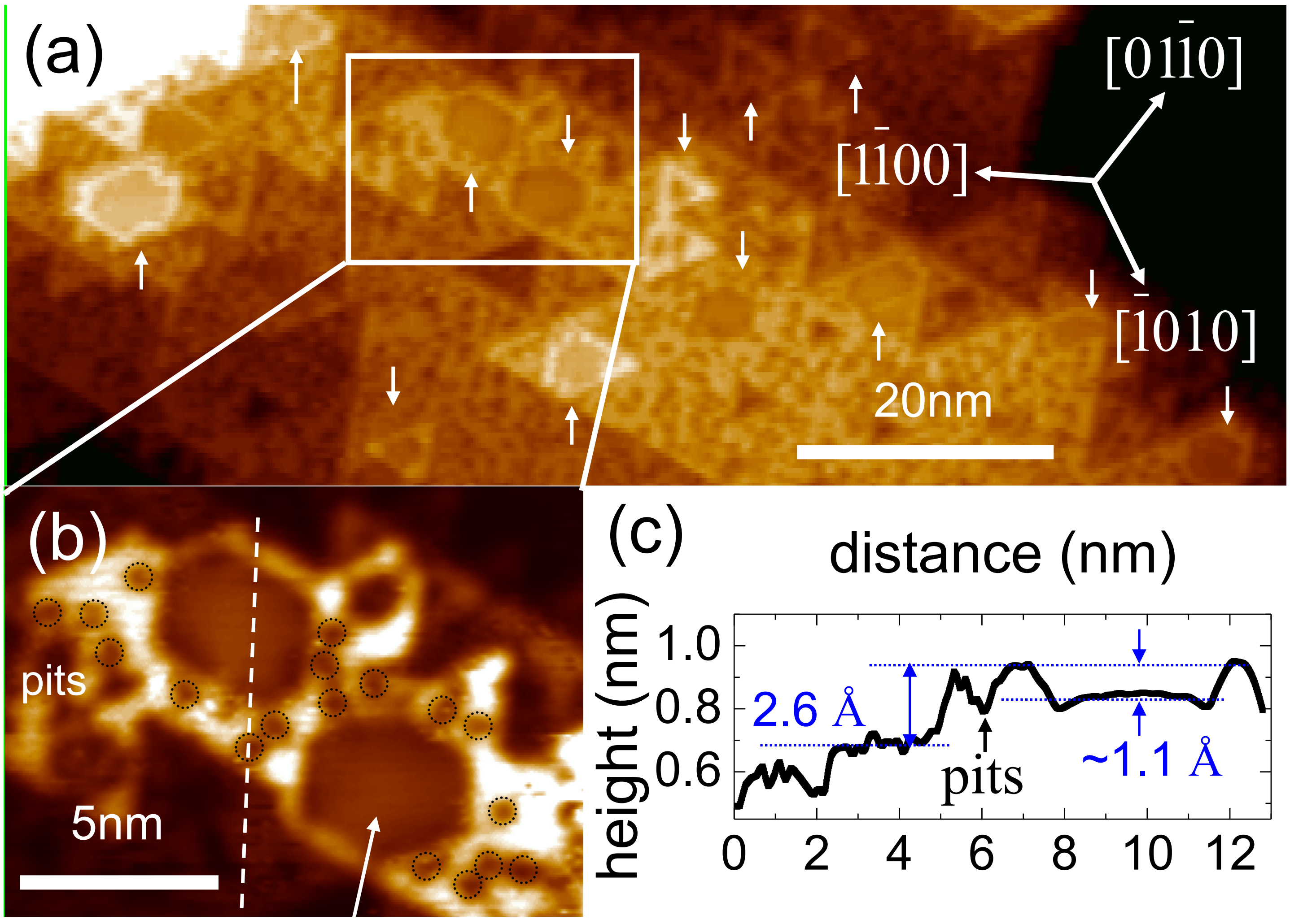
Equipment


AFM & STM chamber: 1×10^{-10} torr
variable temperature: 25K ~ 800K
Preparation chamber: 8×10^{-10} torr
variable temperature: RT ~ 1400K
Ar^{+} Ion-sputtering Gun
Cooling tank:
LN_2 or LHe_2
RHEED E-Gun
Thermal evaporator
RHEED Screen
SPM stage

Initial cleaning surface of (0001)-Zn

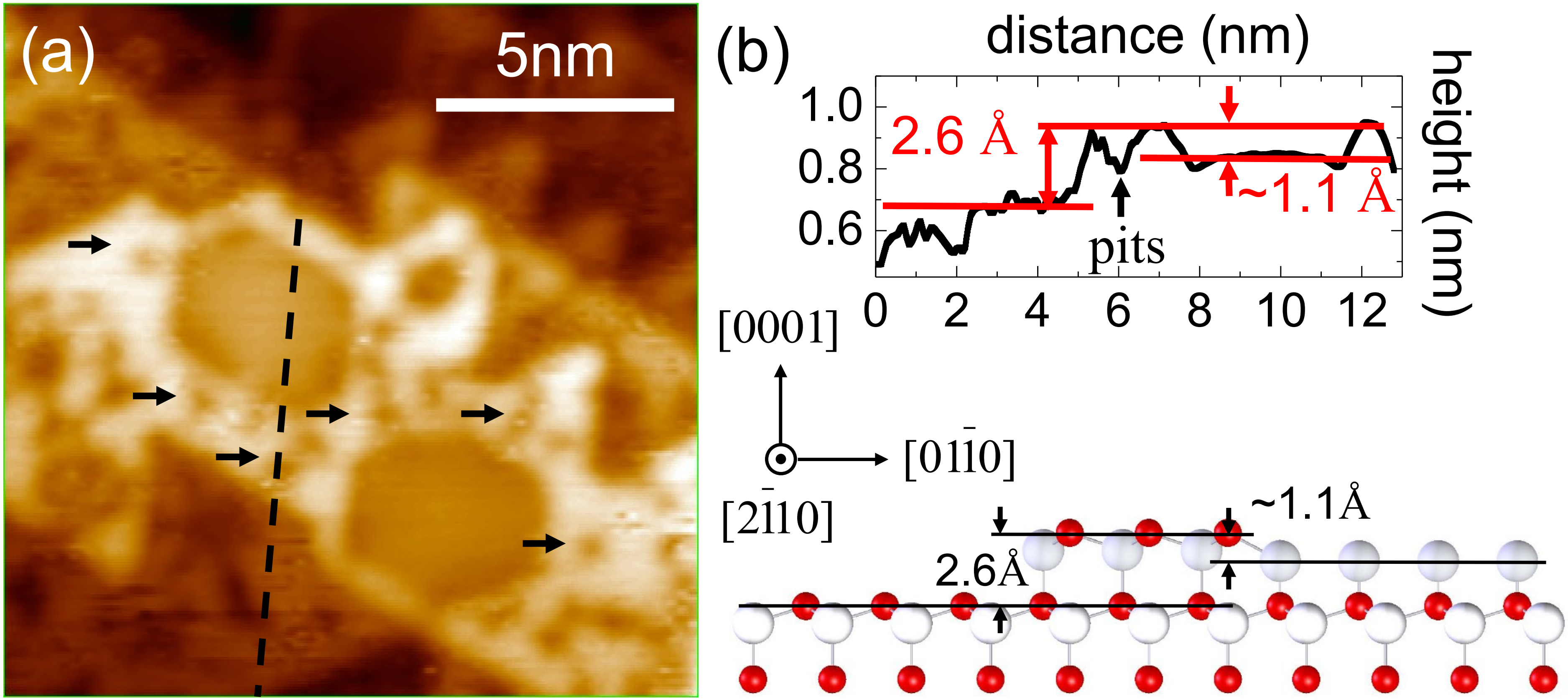


After Ion-bombardment



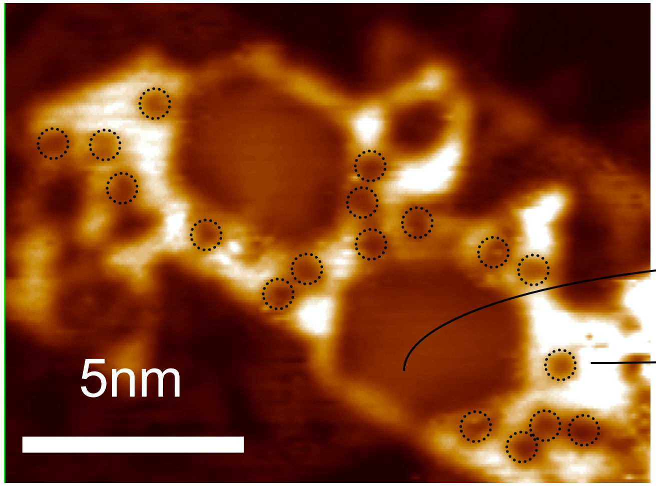
Hexagonal cavities

O-terminated Hexagonal Cavities



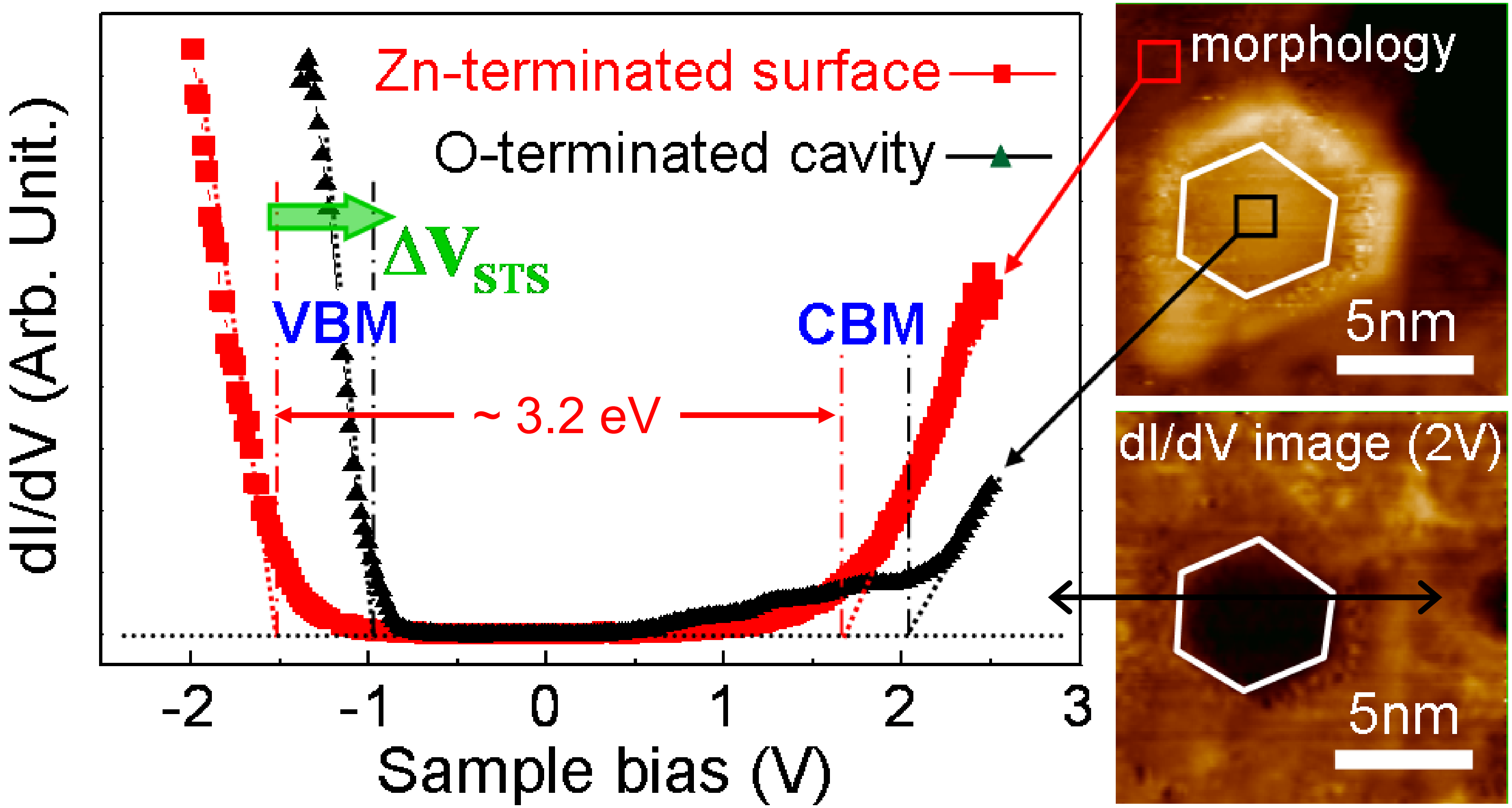
The depth of hexagonal cavities with a diameter of 4 – 5 nm is 1.1 ± 0.2 Å which is much less than one Zn-O double-layer height. The exposed O-terminated surface shows a downward relaxation because of the removal of above Zn atoms. The formation of O-terminated hexagonal cavities results from the collective motion of Zn deficiencies at high temperature.

Electronic & Electrostatic properties of surface defects?



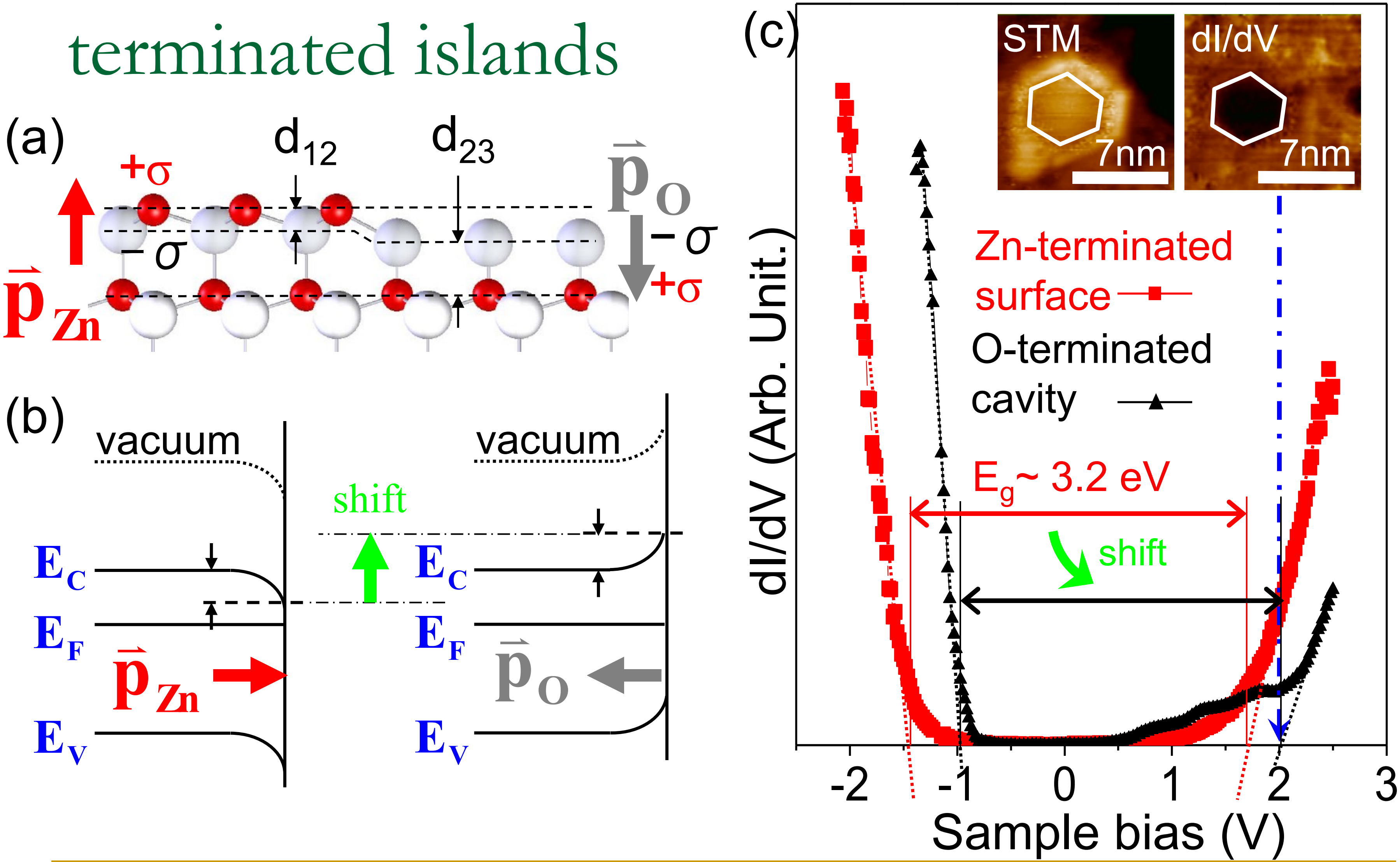
Surface charge ?

Scanning tunneling spectra (STS) for O- and Zn- terminated ZnO(0001) planes



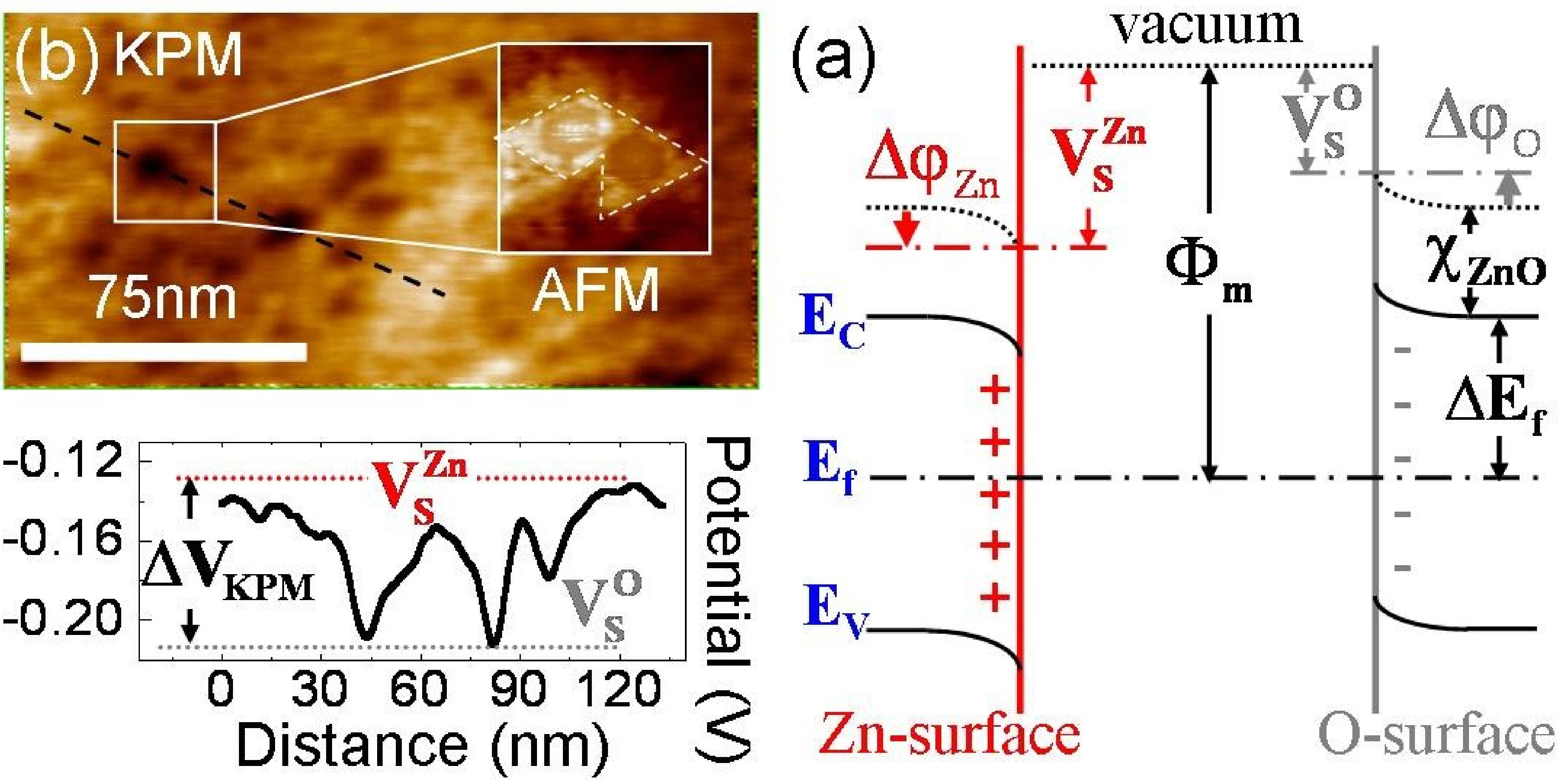
The surface band is modified by surface dipolar field.

STS for O-terminated cavity and Zn-terminated islands



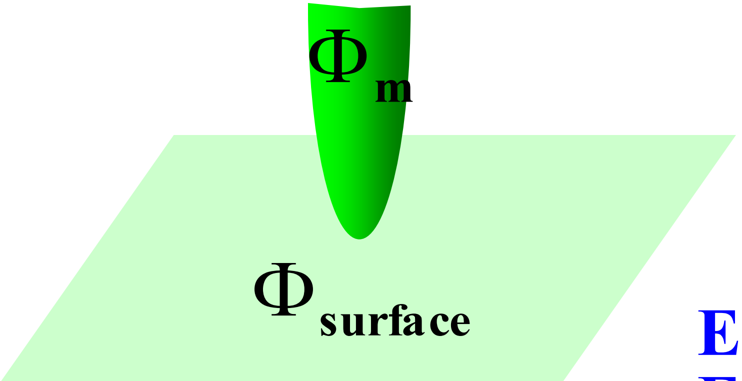
Inversion Surface Dipole Domain

Surface potential distribution of (0001)-Zn by Kelvin probe microscopy (KPM)

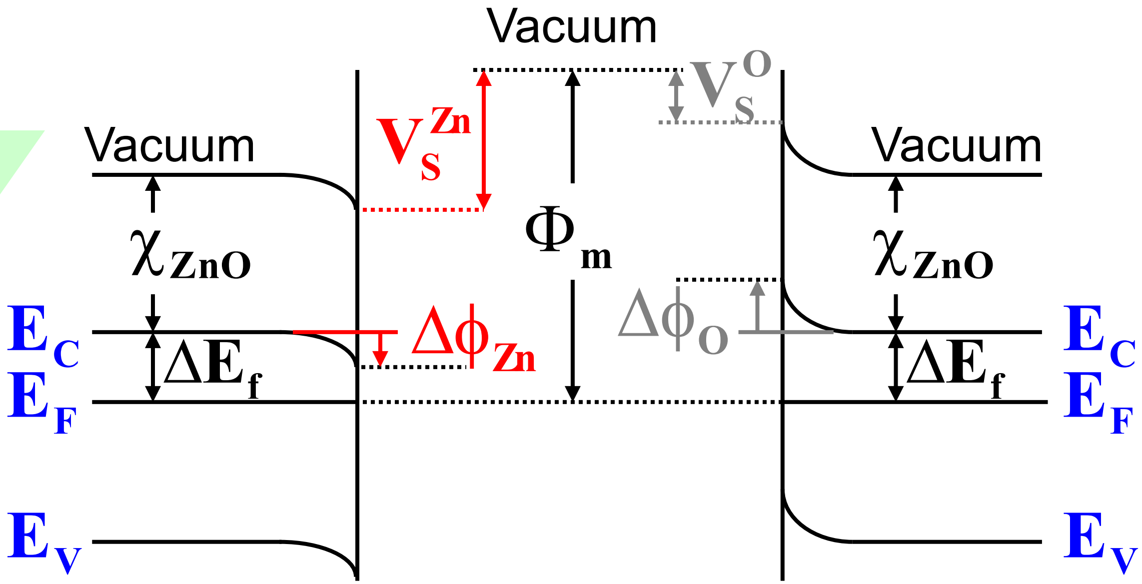


What is the electric charge of the surface defect (pits) ?

Surface contact potential, V_s



$$V_S = \Phi_m - \Phi_{surface}$$



$$V_S^{Zn} = \Phi_m - \chi_{ZnO} + \Delta\phi_{Zn} - \Delta E_f$$

$$V_S^{O} = \Phi_m - \chi_{ZnO} - \Delta\phi_{O} - \Delta E_f$$

$$\Delta V = V_S^{Zn} - V_S^{O} = \Delta\phi_{Zn} + \Delta\phi_{O}$$

Surface dipolar filed effect !!

σ, surface charge density (/cm^2)	$d_{12}+d_{23}$, (Å)	ε, dielectric constant of ZnO	ΔV, surface potential difference (V)
1.5E+13	2.6	8.5 (Buk)	**0.082951147**

Direct Determination of the Interaction between Vacancies on InP(110) Surfaces

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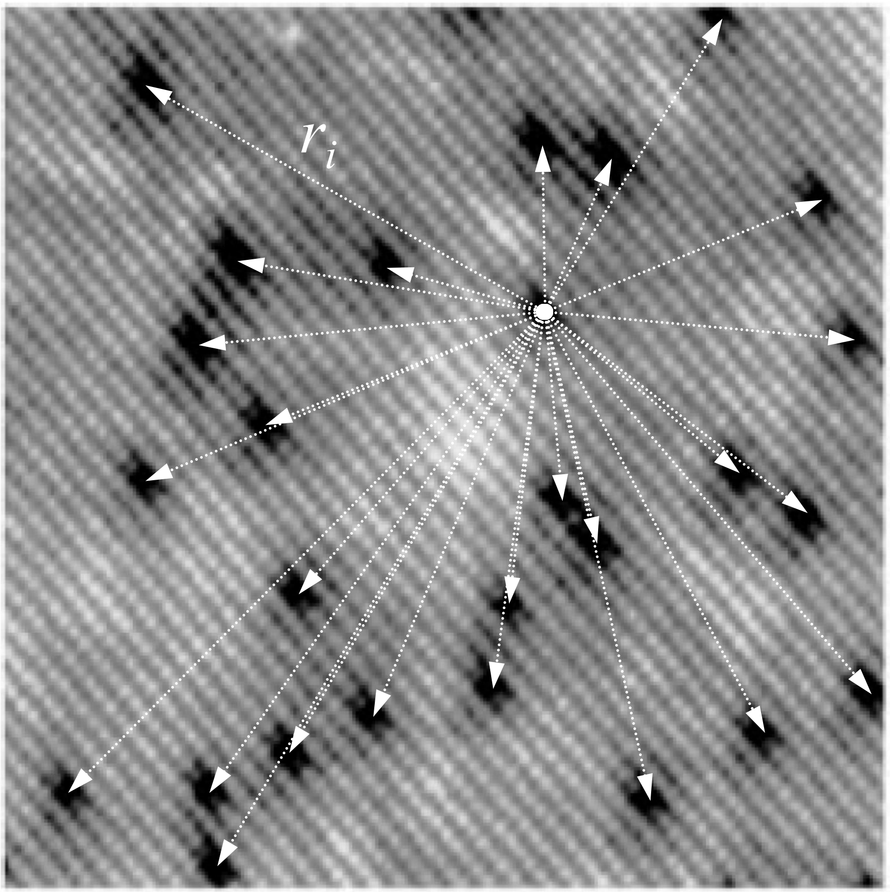


FIG. 1. Scanning tunneling microscope image of thermally formed P vacancies on an InP(110) surface. The image was acquired at -2.6 V tunneling voltage and shows the occupied surface states. The dark spots are the vacancies. Scan width 23×23 nm^2. If the tunneling voltage is changed, a dark zone appears around the vacancy. The magnitude of the depression is a function of the bias voltage and can be used to determine the surface screening length.

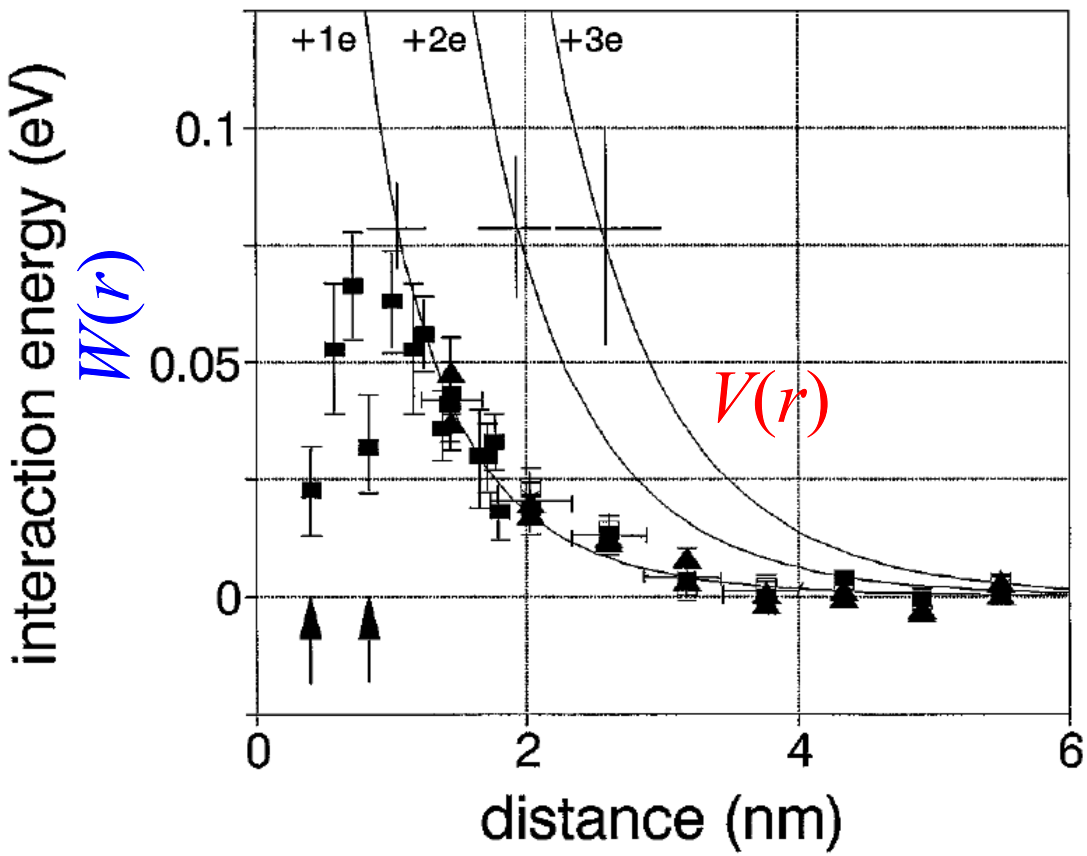
$N(r)$ = # of pair-distance r_i between V_P

$$g(r) = \frac{N(r)}{N'(r)}$$

$N'(r)$: Distribution of r_i in absence of V_P-V_P interaction

$g(r)$: Pair-correlation function

Interaction between P vacancies in InP(110)



Pair-correlation function

$$g(r) = \frac{N(r)}{N'(r)}$$

Mean force potential

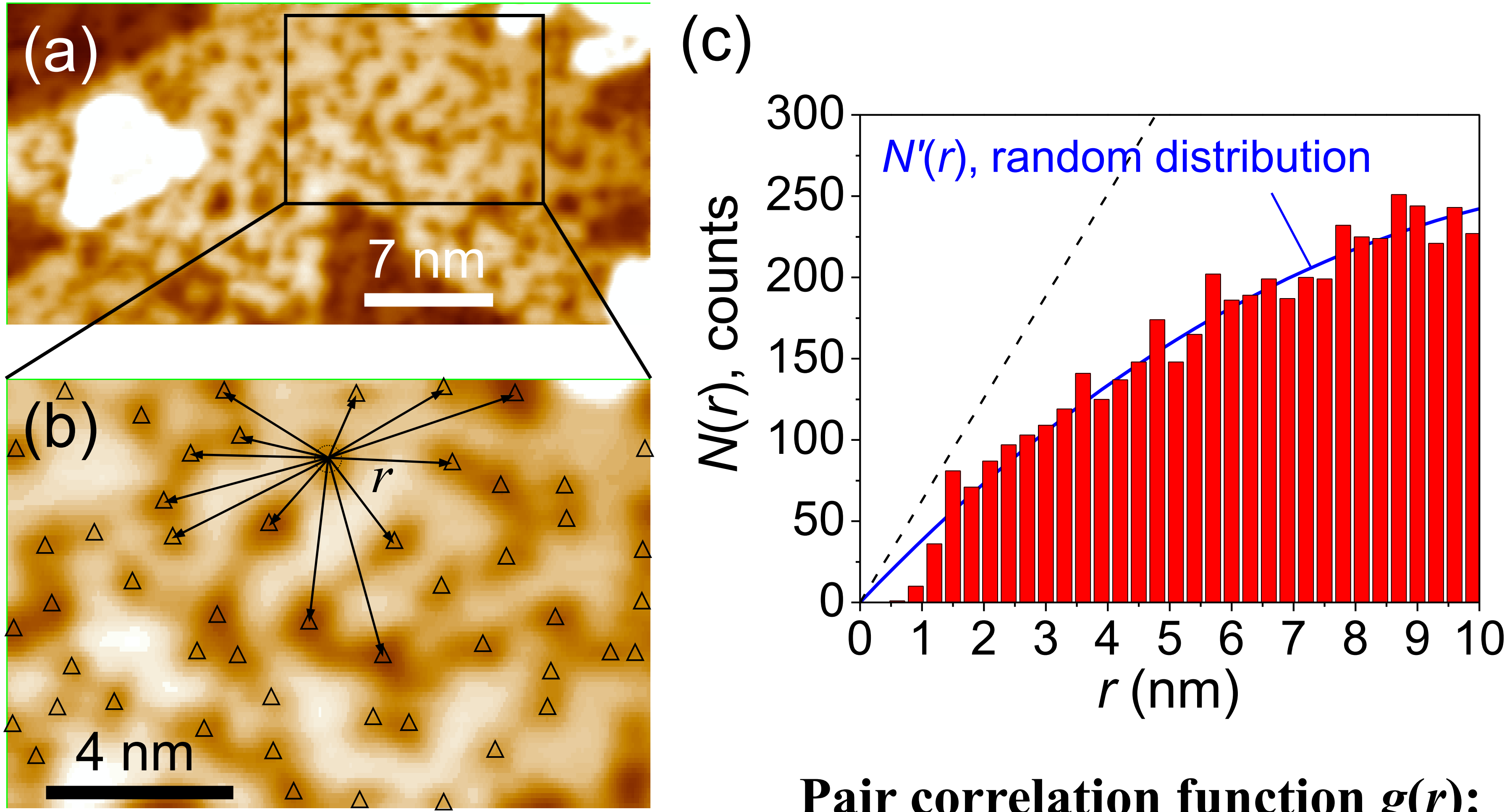
$$W(r) = -kT \cdot \ln[g(r)]$$

Screened Coulomb Potential

$$V(r) = \frac{q}{4\pi\varepsilon_0\varepsilon} \cdot \frac{1}{r} \cdot \exp\left(\frac{-r}{R_s}\right)$$

$R_s = 1.2$ nm, and $q = +1e$

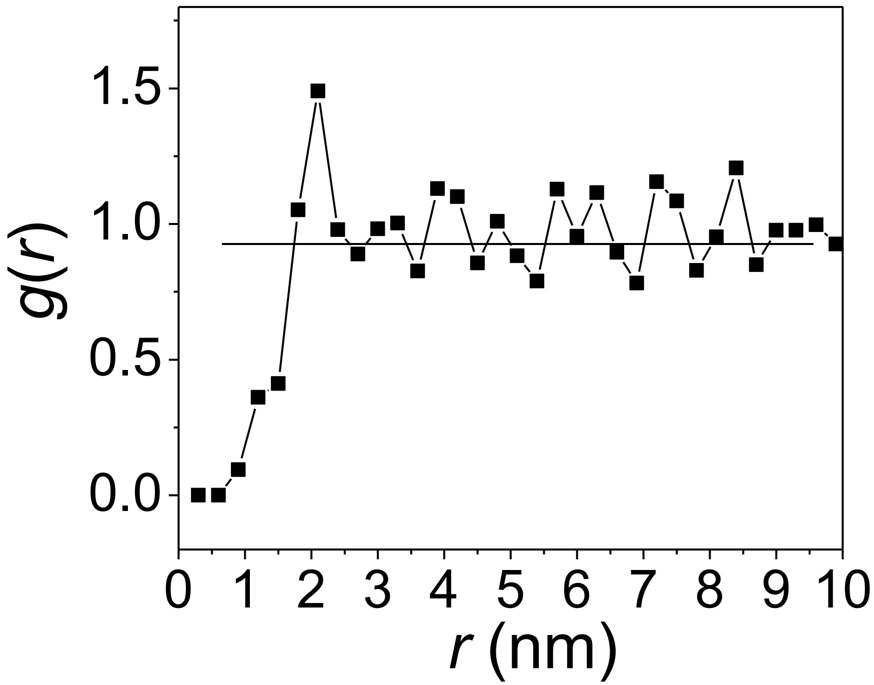
Pair-distribution of pits with charge



Pair correlation function $g(r)$:

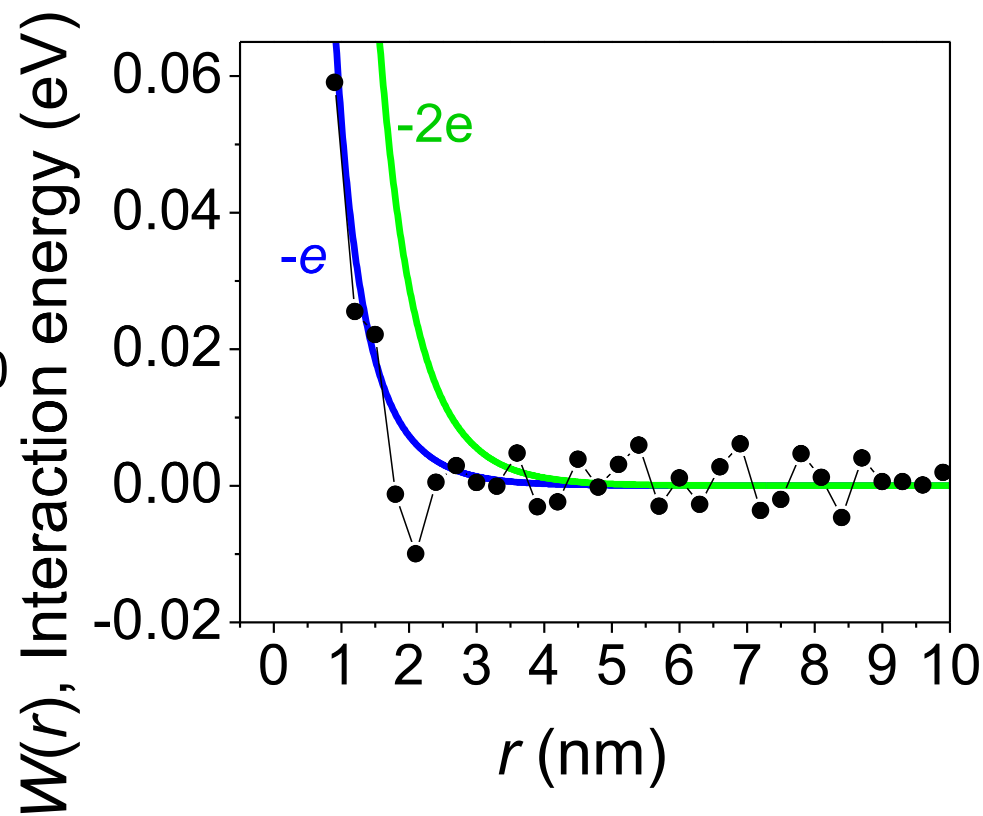
$$g(r) = N(r)/N'(r)$$

Pair-distribution of pits with charge



Mean force potential energy:

$W(r) = -kT \ln [g(r)]$



Screened Coulomb potential energy:

$$V(r) = \frac{q}{4\pi\varepsilon_0\varepsilon} \cdot \frac{1}{r} \cdot \exp\left(\frac{-r}{R_s}\right)$$

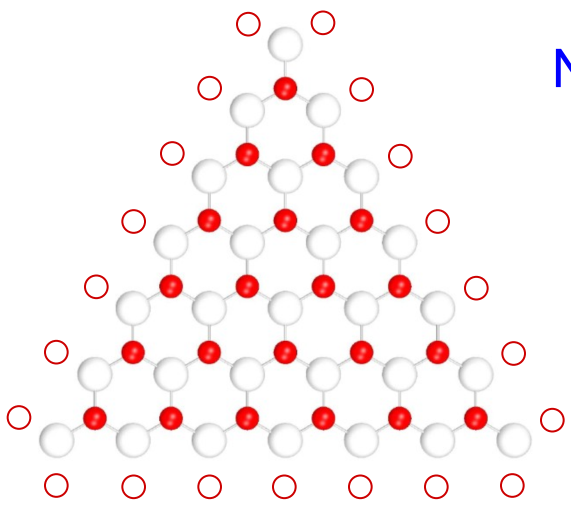
$$R_s = \sqrt{\frac{2\pi^2\varepsilon_0\varepsilon\hbar^3}{e^2 m_e^{3/2} \cdot (2\pi kT)^{1/2} \cdot F_{-1/2}\{E_F/kT\}}}$$

~ 0.8 nm

charge state of $V_{Zn} \sim -1e \pm 0.2\, e$

Stabilizing mechanism with charged surface defects

(Review) Model of Compensation Charge:



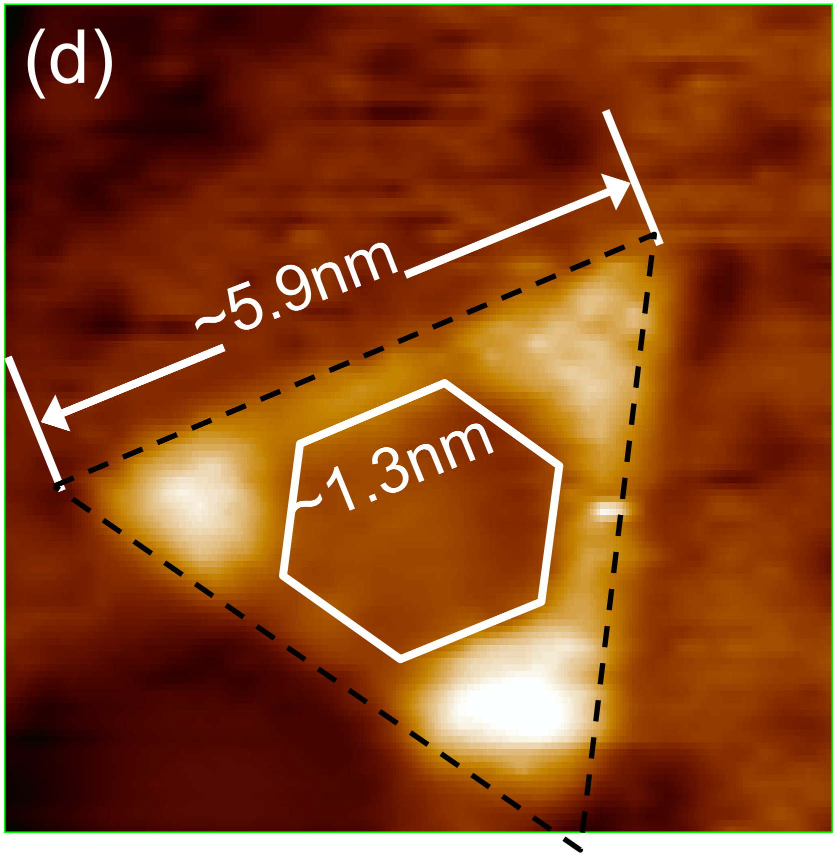
Non-stoichiometry ZnO triangular island

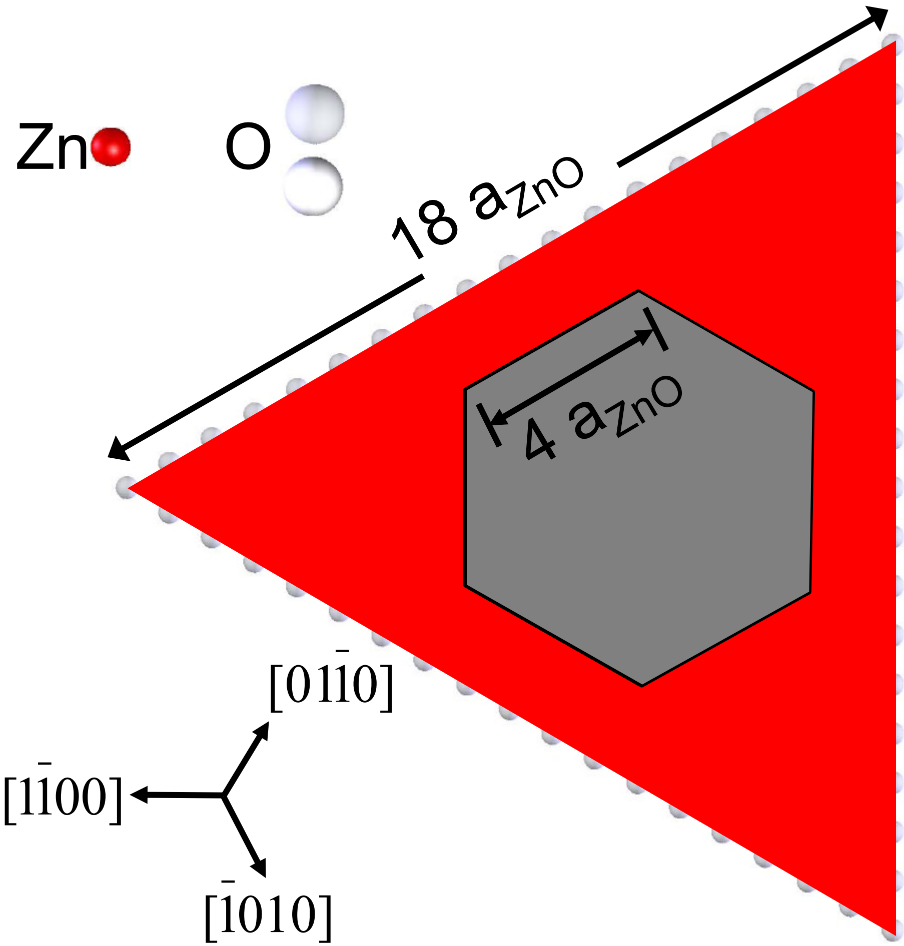
21 Zn : 28 O = 3 : 4

+ 7

compensation charge δ

Ratio of Zn to O for hexagonal cavity on triangular island

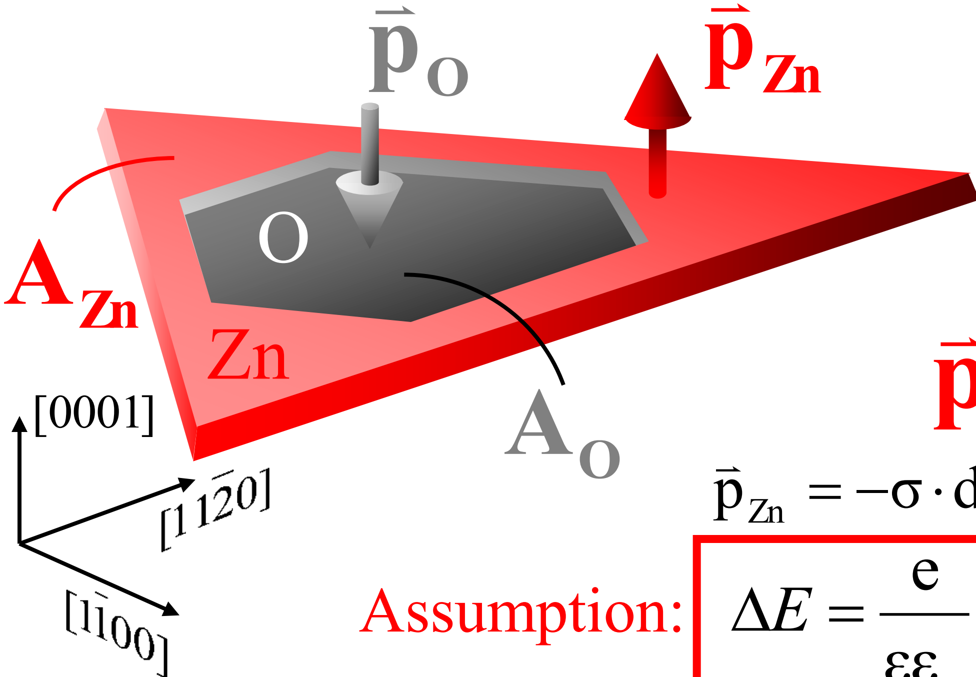


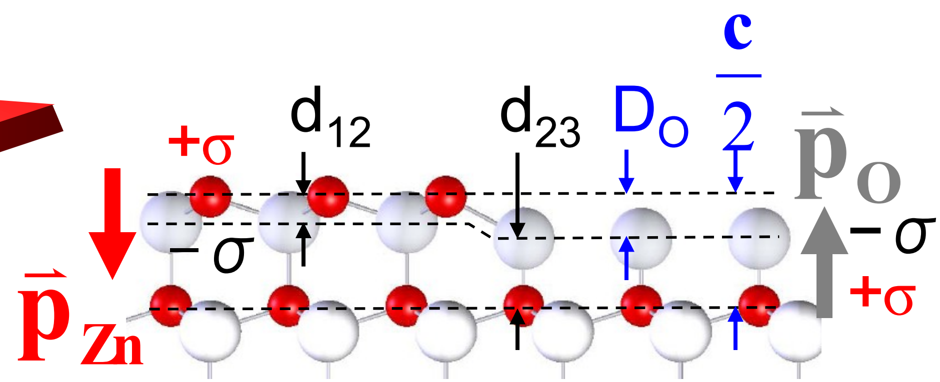


The ratio of Zn and O atoms is 135:191.

The Zn removal is about 30% which departs from the prediction (25%) by Tasker's approach. It implies that there is other pathway to achieve polarity compensation.

Surface relaxation & Inversion surface dipoles





$$\vec{p}_{Zn} = -\sigma \cdot d_{12}\ \hat{z}, \quad \vec{p}_O = \sigma \cdot d_{23}\ \hat{z}$$

Assumption: $\boxed{\Delta E = \frac{e}{\varepsilon\varepsilon_o}\left(\vec{p}_{Zn} \cdot \vec{A}_{Zn} + \vec{p}_O \cdot \vec{A}_O\right) = 0}$

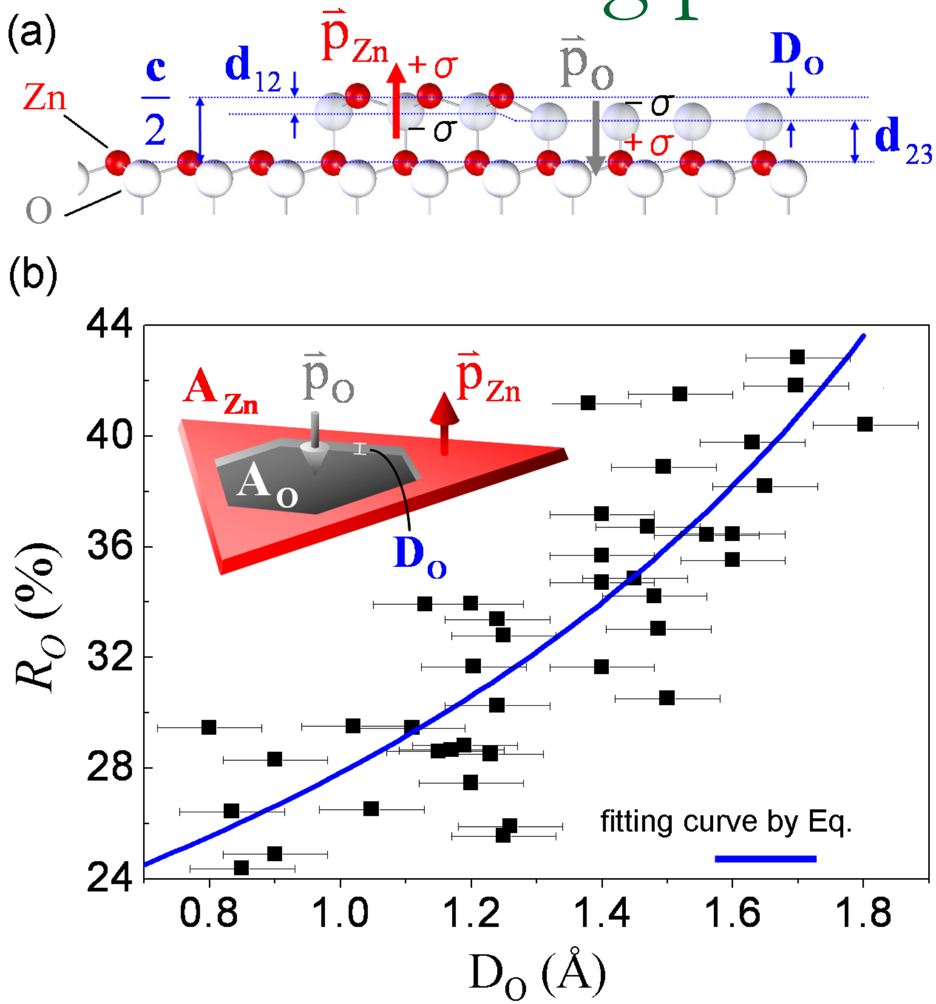
$$\Rightarrow \frac{A_{Zn}}{A_O} = \frac{\vec{p}_O}{\vec{p}_{Zn}} = \frac{d_{23}}{d_{12}}$$

$$R_O = \frac{A_O}{A_{Zn} + A_O} \times 100\% = \frac{d_{12}}{d_{23} + d_{12}} \times 100\% = \boxed{\frac{d_{12}}{\left(\frac{c}{2} - d_O\right) + d_{12}} \times 100\%}$$

Zn removal percentage

Relaxation of O-terminated plane

Statistic analysis of O-terminated cavities & model fitting parameter



Eq.

$$R_O = \left(\frac{A_O}{A_O + A_{Zn}}\right) \times 100\%$$

$$= \frac{d_{12}}{\left(\frac{c}{2} - D_O\right) + d_{12}} \times 100\%$$

fitting parameters

d_{12}=0.6024Å, c = 5.181Å

$\Updownarrow$

d_{12} = 0.65Å, c = 5.207Å

by PRB (67) 035403

The surface defect concentration depended on defect structure can be fitted by this model established by ISDD involving the polar surface stability.

Conclusions

- The surface Zn defects on (0001)-Zn surface can be introduced using annealing & ion-bombardment.
- The surface defects at sub-monolayer depth, including the hexagonal cavities (4 – 5 nm) and small pits (0.5 – 1.2 nm), are the O-terminated surfaces which possess negative charge compared to the Zn-terminated surface.
- The average charge of each surface nanodefect (pit) estimated at (-1*e*) using the pair-distribution analysis.
- We establish a new model "inversion surface dipole domain" that can be used to interpret the stabilization of polar surface.