Supplementary Material (ESI)

I. Detailed Description of Experiments

ZnO microwires grown via CVD method¹ were firstly transferred on a clean (100) Si wafer by two glass tips installed in a micromanipulation system (Olympus). After annealing at 673 K for 30 minutes, the wires were cleaved using two glass tips (Fig. 1(a, b), see video in supplementary material) creating two polar surfaces. *In situ* growth and observation of the polarity-dependent epitaxial growth on cleaved ZnO polar surfaces were carried out in an ESEM (FEI Quanta 200F) equipped with a heating stage (Fig. 1(c)). Mixed gas of argon (10 sccm) and oxygen (0.5/1.0/2.0 sccm) was introduced into the chamber under a pressure of 200 Pa in this work and served as oxygen source during growth. Zinc foil (99.99%) was put near the substrate (two cleaved polar surfaces from one ZnO microwire) in a crucible assembled on the heating stage, which was heated up from room temperature to 973 K at a heating rate of 30 K min⁻¹.

Cleaving process has been often used to create perfect crystal surfaces without mechanical damage caused by other methods, such as polishing, etching and Ar+ sputtering; meanwhile the cleaved surfaces should reveal the equivalent morphology, which ensures the well-controlled substrate conditions. Reliable control experiments can be ensured by the same growth condition on two cleaved micrometer-sized surfaces with close distance between them.

To record the growth rate, growth time was prolonged to over 10 to 100 seconds. During the growth process, each frame of SEM image was obtained in situ every several seconds. The initial epitaxy was determined by morphology changes compared with that observed in the last frame of SEM image.

During growth, ambience in the ESEM chamber maintains a dynamic equilibrium with spatial uniform oxygen distribution. Due to the surface oxidation of zinc piece in an oxygen environment, the evaporation of zinc atoms is restricted by the oxygen concentration. With higher oxygen concentration (or flux), less zinc atoms are generated, and thus, higher oxygen flux leads to lower Zn/O ratio.

II. Detailed DFT Simulation Method

DFT simulations were preformed to investigate the physical mechanism of the experimentally observed polarity-dependent epitaxial growth on ZnO polar surfaces. We carried out total-energy calculations and geometry optimizations for supposed surface atomistic configurations employing DFT within the generalized gradient approximation (GGA). We used the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE) and the program package DMol3 implemented in Materials Studio (Version 4.3) of Accelrys Inc.^{2, 3}. In this work we focused on the polarity effects and used clean polar surfaces without reconstructions and absorptions in simulations.

For our calculation, slabs consisting of four Zn-O double layers were constructed for modeling both (0001)-Zn and (0001)-O surface in the periodical supercell mode (4×4 lateral supercell (32 atoms per layer)), which were separated by a vacuum region of 20Å thick. Atoms in the bottom two layers were fixed in their original bulk coordinates before geometry optimizations and the upper two layers were allowed to relax. Meanwhile, we tested the effects of slab thickness and hydrogen-passivation of

bottom atoms. The systematic error induced by uncompensated polarity⁴ could be eliminated for adsorption configurations on (0001)-Zn surface by averaging the calculated energies of the slabs with and without H-passivation for the same thickness; while for $(000\bar{1})$ -O surface these effects had little impact on the energy calculation. In our calculations, to search the minima of adsorption configurations, the hypothetical nuclei were placed above the as-optimized polar surfaces in several presumptive positions.

In the ZnO growth process of our CVD experiments, oxygen gas was introduced and zinc vapor was supplied by evaporation of zinc foil at the temperature of about 1000K. Thus, with reference to DFT energies of zinc atom (E_{Zn}) and oxygen molecule (E_{O_2}), considering the effect of spin polarization), the binding energy of surface adsorbate with n_{Zn} Zn adatoms and n_0 O adatoms (Fig. S4) can be calculated by

$$E_{\text{binding}} = (E_{\text{ads}} - E_{\text{surf}}) - n_{\text{Zn}} E_{\text{Zn}} + \frac{1}{2} n_{\text{O}} E_{\text{O}_2}$$

where E_{ads} and E_{surf} represent DFT total energies for the simulated ZnO monomer adsorption configuration and clean surface, respectively. In addition, for the simulation in the ambience of O atoms, the binding energy should be written as

$$E_{\text{binding}} = (E_{\text{ads}} - E_{\text{surf}}) - n_{\text{Zn}} E_{\text{Zn}} + n_{\text{O}} E_{\text{O}}$$

where E_0 is DFT energy of oxygen atom. The calculating results are summarized in Table S1.

Dissociative chemisorptions of O_2 on polar surfaces are simply simulated by DFT geometry optimization of O_2 molecule incorporated structures. The minimum requirements for breaking the oxygen double bond are illustrated in Fig. S5.



Fig. S1 Several segments cleaved from one microwire show similar epitaxial structures grown in the same polarity direction (a-c). Segment (a) is not the cleaved from (b) but in the same direction. (b) is the other end of the left segment in (c). The right segment in (c) is just cleaved from the left one. Scale bar for (a-c): 500 nm. White dotted lines denote the epitaxial boundaries.



Fig. S2 High resolution TEM characterization of $(000\overline{1})$ -O epitaxial surface with the corresponding diffraction pattern in the inset. The blurry diffraction ring in the pattern is attributed to the Pt polycrystal layer. No amorphous layer or grain boundary can be found, which shows a perfect epitaxial growth front.



Fig. S3 (a-c) In-situ observation of epitaxial growth under 0.5 sccm O_2 flux of a cleaved (0001)-Zn surface starting from the reference 0 s to 46 s with the temperature rising from 904 K to 924 K synchronously. After growth the epitaxial structure on (0001)-Zn surface (d) was observed by SEM; The corresponding (0001)-O surface (e) showed little growth. White dotted line in (d) denotes the epitaxial boundaries.



Fig. S4 Surface absorption configurations with minimal total energy on both polar surfaces according to DFT simulations. (a, b) One ZnO monomer and O adatom absorbed on (0001)-Zn surface, respectively. (c-g) One ZnO monomer, one Zn adatom, two ZnO monomers, two Zn adatoms and three ZnO monomers adsorbed on $(000\bar{1})$ -O surface. The corresponding binding energies of configurations (a-f) are listed in Table S1.



Fig. S5 Dissociative chemisorptions of O_2 on polar surfaces. (a) Stable adsorption of one Zn adatom on (0001)-Zn surface with an O_2 molecule incorporated near the structure before DFT geometry optimization. (b) The atomistic structure after optimization of (a). (c, d) Another incorporation configuration of O_2 molecule before optimization and the final optimized structure on (0001)-Zn surface. (e) Unstable adsorption of three adjacent Zn adatoms at near lattice positions on (0001)-O surface with an O_2 molecule incorporated in the most probable position before optimization. (f) The atomistic structure after optimization of (e). (g, h) Another adsorption configuration of Zn adatoms with O_2 molecule incorporated before optimization and the final optimized structure on (0001)-O surface. The structures shown above are the minimum requirements for breaking the oxygen double bond on the basis of necessary simulations (not shown here) of structure evolution, where oxygen double bond cannot be broken spontaneously.

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Surface	Binding energy/eV				
	One ZnO Monomer	Two ZnO Monomers	One Zn Adatom	One O Adatom	Two Zn Adatoms
(0001)-Zn	4.2 ^{<i>a</i>}			3.4 ^{<i>a</i>}	
(000Ī)-O	2.0 ^{<i>a</i>} /5.1 ^{<i>b</i>}	7.3 ^{<i>a</i>}	3.4 ^{<i>a,b</i>}		6.4 ^{<i>a</i>}
Note: The desorption energy is calculated from the relevant binding energies:					
Desorption of Zn adatom from one monomer adsorbed on (0001)-Zn surface: 0.8 eV;					
Desorption of O adatom from one monomer adsorbed on $(000\overline{1})$ -O surface: -1.4 $a/1.7$ eV;					
Desorption of two O adatoms from one two monomer adsorbed on (0001)-O surface: 0.9 eV.					
^{<i>a</i>} calculation for O_2 molecules ambience; ^{<i>b</i>} calculation for O atoms ambience					

Table S1 DFT calculated parameters for relevant binding energy

References

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