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From the absolute surface energy to the stabilization mechanism of high index polar surface in wurtzite structure: The case of ZnO

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ABSTRACT

An improved wedge-shape method is employed to calculate the absolute surface energies of wurtzite ZnO high index polar surfaces. From the viewpoints of atomic structure and surface energy, the stabilization mechanism of high index polar surfaces is systematically investigated. Under different conditions (O and Zn rich), the stable surface structures are discussed, and it is found that some high index polar surfaces may have lower surface energy than conventional $(10\bar{1}0)$ or (0001) surfaces. This may be of vital importance to the surface morphology of nanostructures. In addition, the calculation results are well in agreement with experimental observations. The present theoretical and experimental work can provide important insights to the growth and surface treatment of complex nanostructures.

1. Introduction

Wurtzite (WZ) semiconductors and their nanostructures are of great interest for broad applications in modern microelectronic industry [1–3]. GaN and ZnO are typical materials with WZ structure. The direct and wide band gap make them extremely important for optoelectronic and high-power devices [4–7]. In the case of ZnO, due to its large exciton binding energy at room temperature, high breakdown strength and saturation velocity, it has attracted much attention for potential applications in UV sensors and high efficiency light emission [8–10].

Nanostructures have many so-called "Nano-effects" which can lead to more excellent physical and chemical properties with respect to their bulk counterparts [11,12]. For most nanostructures, their performances highly depend on the surface morphology [13]. It is believed that surface-controlled process of nanostructures would provide an effective path to meet the diverse requirements of future device application. For example, it has been demonstrated that structures with high index polar surfaces usually have high energy but much better catalytic performance in TiO_2, Cu_2O, SnO_2 and $SrTiO_3$ materials [14–20]. For ZnO, Han et al. also found that the order of gas sensing and photocatalytic efficiency of ZnO are sensitive to the index and polarity of the surfaces, and the higher the better [21]. Therefore, related researches on the feasible fabrication of high index surfaces are the most urgent needs for the recent ZnO-based applications. However, constrained by the crystal equilibrium theories such as Gibbs-Wulff law [22] and energy minimization principle [23], the nanomaterials are always decorated with low index surfaces, such as $(10\bar{1}0)$ (*m* surface), $(11\bar{2}0)$ (*a* surface) and (0001) (*c* surface) surfaces [24–26]. It is a big challenge to prepare nanostructures with diverse surfaces via the conventional synthesis strategies. In recent years, with the development of technology in crystal growth and surface modification, some special kinds of ZnO nanostructures enclosed by high index polar are synthesized and characterized. Han et al. firstly reported a liquids-growth and wet-chemical etching technique [27]. The

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smooth ZnO nanorods (NRs) decorated by *m* surface were converted into pagoda-like or dumbbell-like ones decorated by (0001) and $(10\bar{1}1)$ surfaces. Other types of WZ nanostructures decorated by high index polar surfaces, such as tubes [28], flakes, rods and wires [29,30] have been fabricated using various deposition or post-treatment methods [8,31–33]. In contrast with experimental studies, the theoretical investigations about stabilization mechanism of the high index polar surfaces are still lacking.

In this work, based on first-principles method, an improved wedge-shape method is proposed to calculate the absolute surface energies of high index polar surfaces in WZ structure. In the case of WZ ZnO, the detailed surface structures and surface energies of high index polar surfaces are systematically investigated under different chemical conditions. We found that under special conditions (O or Zn rich) there is a certain high index polar surface with reconstruction, corresponding to the lowest surface energy. This ought to be the main reason for those various morphologies of ZnO nanostructures. In addition, the observations in our experiment can be well explained by the theoretical results, indicating that our work is significant to understand the stabilization mechanism of high index polar surfaces.

2. Methods and computational details

The first principles calculations based on density functional theory (DFT) were performed by the Vienna Ab initio Simulation Package (VASP) code with a plane wave basis set [34–36]. The generalized gradient approximation (GGA) with PBE function was employed as the exchange correlation functional [37]. The energy cut off of plane wave basis set was taken to be 500 eV. All the atoms in the models were allowed to relax until forces converged to less than 0.02 eV/Å. A gamma-center *k* point mesh was used and the *k* number was meticulously designed for every model. The oxygen molecule was calculated with considering spin polarization. The thickness of vacuum layer was set to be at least 12 Å.

In our work, an improved wedge-shape method is employed to calculate the absolute surface energies of wurtzite ZnO high index polar surfaces. Conventionally, the surface energy can be calculated by a slab geometry [38]. In the case of ZnO, the sum of the top (t) and bottom (b) surface energies σ^{t+b} is defined as

$$\sigma^{t+b} = [E_{tot}(slab) - n_{Zn}\mu_{Zn} - n_O\mu_O]/A, \quad (1)$$

where $E_{tot}(slab)$ is the total energy of the slab supercell. $n_i (i = \text{Zn and O})$ is the number of *i*th atom in the supercell and μ_i is the chemical potential of *i*th atom. *A* is the surface area. Setting $E_{tot}(Zn)$ *(and O)* to be the energy of element solid Zn (and half of gas O_2), and $\Delta H_f(ZnO)$ to be the formation enthalpy of a bulk ZnO, one can have [39].

$$\mu_{Zn} = E_{tot}(Zn) + E_{tot}(O) + \Delta H_f(ZnO) - \mu_O, \quad (2)$$

$$E_{tot}(Zn) + \Delta H_f(ZnO) \leq \mu_{Zn} \leq E_{tot}(Zn). \quad (3)$$

Eqs. (2) and (3) means thermal equilibrium between surface and bulk. For non-polar surfaces, one can cut a slab with two identical surfaces

$$\sigma^t = \sigma^b = 1/2\sigma^{t+b}. \quad (4)$$

It is worthwhile mentioning that some polar surfaces such as (001) in ZB ZnO also can be calculated by Eq. (4), because it is also possible to construct a slab such that Eq. (4) holds. However, it is impossible to apply this method to other polar surfaces because of the absence of symmetry. To address this important issue, several attempts have been made to calculate the surface energies of polar surfaces [7,40]. S. B. Zhang et al. suggested a wedge-shaped geometry to separate the absolute surface energies of (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces for ZB structures [40]. As shown in Fig. 1(a), the wedge geometry should consist of two equivalent (111) passivated surfaces and one (001) passivated surface. Because the surface energy of (001) surface in ZB structures can be obtained directly by slab geometry, the individual surface energy of (111) passivated surface thus can be separated. In order to remove the contribution of three ridges, two similar wedge geometries with different sizes *n* should be constructed, where *n* is defined by the number of Zn atoms on side edge of the wedge geometry in Fig. 1, Thus,

$$\begin{aligned}\delta E &= E_{tot}(n) - E_{tot}(n-1) - nE_{tot}(ZnO) \\ &= 2\sigma_{(111)} + \sigma_{(001)},\end{aligned} \quad (5)$$

σ is renormalized to the energy of per 1 × 1 surface area, $E_{tot}(n)$ is the total energy of wedge geometry and $E_{tot}(ZnO)$ is the energy of a bulk ZnO. Unfortunately, this method can't be applied directly for polar surfaces in WZ structures due to their low symmetry. L. Hong et al. have used this method to calculate the relative surface energies of polar and semipolar surfaces for WZ GaN. However, the absolute surface energies of them have not yet been obtained [41]. Recently, based on this method, J. Z. Zhang et al. made significant attempt to calculate the absolute surface energies of polar (0001)/ $(000\bar{1})$ surfaces for WZ ZnO [7]. In their work, WZ (0001)/ $(000\bar{1})$ surfaces were substituted by ZB (111)/$(\bar{1}\bar{1}\bar{1})$ surfaces. In general, it is acknowledged that [42] (I) the formation enthalpies of ZB and WZ ZnO (or GaN) are similar; (II) the surface atoms on the ZB (111) /$(\bar{1}\bar{1}\bar{1})$ surfaces have the same circumstance and structures as the WZ (0001)/$(000\bar{1})$ polar surfaces. Therefore, the ZB (111)/$(\bar{1}\bar{1}\bar{1})$ surfaces are adopted as reasonable approximations to simulate the WZ (0001)/ $(000\bar{1})$ surfaces.

In this work, to calculate absolute surface energies of high index polar surfaces in WZ structures, wedge geometries consisting of a passivated (0001) surface and two equivalent high index polar

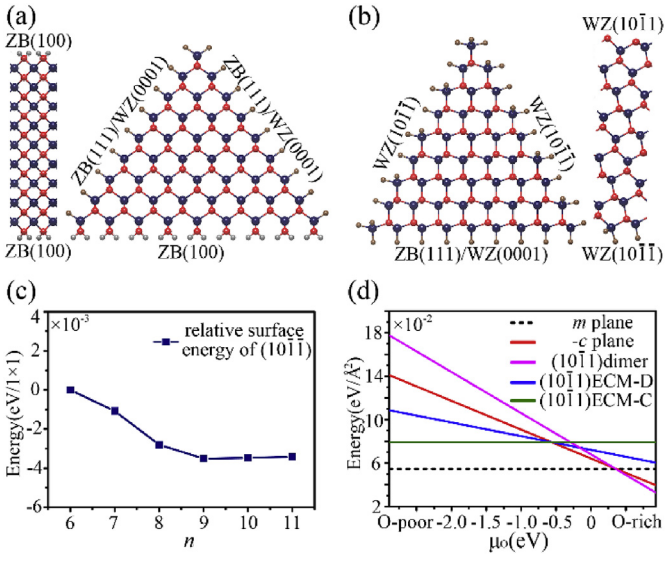

Fig. 1. Cross sectional view of the ZnO slab and wedge geometries for calculating surface energies of (a) passivated ZB (100) and ZB(111)/WZ(0001), (b) passivated WZ(10$\bar{1}\bar{1}$) and original WZ(10$\bar{1}$1). Zn is the blue ball, and O is the red ball. The surface is passivated by H0.5 (small-silvery ball) and H1.5 (small brown ball). (c) The calculated (10$\bar{1}\bar{1}$) relative surface energy as a function of the size n in Eq. (6). The energy zero is set at n = 6. The surface is passivated by H1.5. (d) The calculated individual surface energies as a function of the Zn atom chemical potential for m, -c surfaces and two kinds of ECM (10$\bar{1}$1) surfaces. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)