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Intrinsic magnetic properties of ZnO nanoislands: Insight from first-principles study

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ABSTRACT

First-principles calculations have been employed to investigate magnetic and electronic properties of monolayer and multi-layer ZnO nanoislands which are hexagonal BN (h-BN) prototype structures with zigzag edges and a triangular form. Two types of the zigzag edges, that is, O-terminated and Zn-terminated ones are considered. It has been found that monolayer ZnO nanoislands with the O-terminated edges exhibit magnetic properties, regardless of the nanoislands size. However, the nanoislands with Zn-terminated edges are semiconductors, and the magnetic properties are observed just for some specific sizes. Charge transfer according to Bader charge analysis is introduced to elucidate the magnetic properties of the monolayer ZnO nanoislands. Besides, multi-layer ZnO nanoislands exhibit magnetic features when their layers are odd, while those of even layers are nonmagnetic.

1. Introduction

Zinc Oxide (ZnO), as a typical compound of II–VI group, is an important semiconductor with wurtzite structure as its most stable configuration in the natural conditions. Due to the extraordinary properties of good transparency, wide direct band gap, and large exciton binding energy, ZnO has been applied in emerging applications for transparent electrodes, solar cells, and blue/ultraviolet light emitting devices. Over the past decades, low dimensional ZnO nanostructures with various morphologies, such as nanowires [1], nanotubes [2], nanobelts [3], nanorings [4], and nano-polyhedral cages and shells [5], have been synthesized successfully in the experiments. Some of them have been applied in optical devices owing to their distinguished performance in electronics, optics and photonics [6–10].

Recently, ZnO (0001) monolayers with a hexagonal BN (h-BN) prototype structure have been successfully fabricated and explored for their potential applications in electronic devices [11–13]. Extensive theoretical studies have confirmed that a phase transformation from wurtzite to the h-BN structure could be observed in ZnO films when their thickness is less than 18 layers or so [12–15]. Similar structural transformation is also discovered in ZnO nanowires and nanoclusters [16–18]. Motivated by the experiment [11], low-dimensional ZnO nanostructures such as monolayer sheets and nanoribbons, have also attracted considerable attentions [19–21]. It has been found that zigzag ZnO nanoribbons can exhibit metallic and magnetic features without any edges passivation [20,21], as well as half-metallic ferromagnetism when only edge Zn atoms are saturated by H atoms [22]. Through the analysis of charge and spin densities, these metallic and magnetic features in the zigzag ZnO nanoribbons are determined by O-dominated edges displaying unpaired spins. Of particular interest is that by removal of surface Zn atoms, triangular shaped ZnO nanoislands with O-terminated edges can be formed and stabilized on ZnO(0001)–Zn surface [23]. These "magic" nanoislands are one-layer thick with side lengths ranging from 16 to 34 Å. In addition, monolayer graphene, BN, and SiC nanoislands with multiple shapes have also been paid great efforts because of their unique flexible tunability of magnetic properties [24–27]. Thus, it is naturally expected to explore what will occur in the case of ZnO nanoislands. Unlike the graphene nanoisland, ZnO nanoisland is a metal oxide and its edges terminated by O or Zn atoms will result in different electronic properties, and further affect the functionality and applications. To our best knowledge, however, electronic properties of monolayer and multi-layer ZnO nanoislands with different sizes and edge terminations remain unknown.

In this paper, we will employ density functional theory (DFT) calculations to investigate magnetic and electronic properties of zigzag ZnO nanoislands with a triangular form. Different edge terminations and sizes are considered. Similar to ZnO nanoribbons, ZnO nanoislands with O-terminated edges are metallic and

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ferromagnetic properties, whereas Zn-terminated nanoislands exhibit nonmagnetic. In addition, armchair ZnO nanoislands with the same triangular form are also explored and predicted to be nonmagnetism. Therefore, the focus of the present work is solely on the zigzag ZnO nanoislands. Our article is constructed as follows. A brief description of computational methodology is given in the following section. Section 3 presents calculated results, discussion and comparison with available studies. Main conclusions are summarized in Section 4.

2. Computational methodology

First-principles calculations based on the spin-polarized density functional theory (DFT) within the projected augmented wave method, as implemented in the Vienna *ab initio* simulation package (VASP) [28–30], have been employed to investigate magnetic and electronic properties of ZnO nanoislands (ZnONIs). The exchange correlation interactions are described by the functional of Perdew and Wang 91 (PW 91) within generalized gradient approximation (GGA) [31]. Zn $3d^{10}4s^2$ and O $2s^2 2p^4$ are treated as valence electrons. The cut-off of plane-wave energy is set to 500 eV, and the convergence for total energy is controlled to be smaller than 10^{-6} eV. $1 \times 1 \times 1$ k-point mesh is adopted to describe the Brillouin-zone integrations.

Since electronic properties of low-dimensional nanostructures strongly depended on their sizes and atomic edge configurations, two types of zigzag ZnONIs with a triangular form are considered in this work: (i) ZnONI with O-terminated edges (denoted as O_n–ZnONI, where the index n represents the corresponding size of ZnONI) and (ii) ZnONI with Zn-terminated edges (denoted as Zn_n–ZnONI). In addition, multi-layer ZnONIs (containing bi-layer, tri-layer, four-layer, and five-layer ones) with the size of $n = 3$ have also been investigated. All ZnONIs are modeled in a large rectangular supercell with the periodic boundary conditions. To eliminate interaction between neighbor ZnONIs, a vacuum region of at least 10 Å is applied along three-dimensional directions of the rectangular supercell. Geometrical optimizations are performed by computing the Hellmann–Feynman (H–F) forces using the conjugate gradient algorithm [32]. All atoms in the supercell are allowed to fully relax until the H–F force on each atom is smaller than 0.005 eV/Å.

3. Results and discussion

Structural and electronic properties of monolayer ZnO sheet are investigated firstly. After the full geometrical relaxation, initial buckled ZnO sheet constructed from wurtzite bulk is transformed into a flat one. All atoms prefer to form a threefold coordinated planar sheet rather than a fourfold coordinated configuration, like monolayer BN sheet. The optimized lattice constant and Zn–O bond length are 3.284 and 1.896 Å, respectively. Spin-polarized DFT calculations show that the monolayer ZnO sheet is nonmagnetic semiconductor with a direct band gap of 1.68 eV at Γ point. All the results above are well consistent with the previous studies [13,15,19,33], which indicates our present approaches are valid to explore ZnONIs.

3.1. Monolayer ZnONIs

Monolayer O_n–ZnONI and Zn_n–ZnONI with size n from 2–7 are investigated. The size $n = 2$ to 7 corresponds to the lengths ranging from 6.625 to 23.456 Å, which can be compared to the experimental data [23]. As a typical example, initial monolayer O_6–ZnONI and Zn_6–ZnONI are shown in Fig. 1. Similar to monolayer ZnO sheet, the fully optimized ZnONIs also prefer flat geometrical structures.

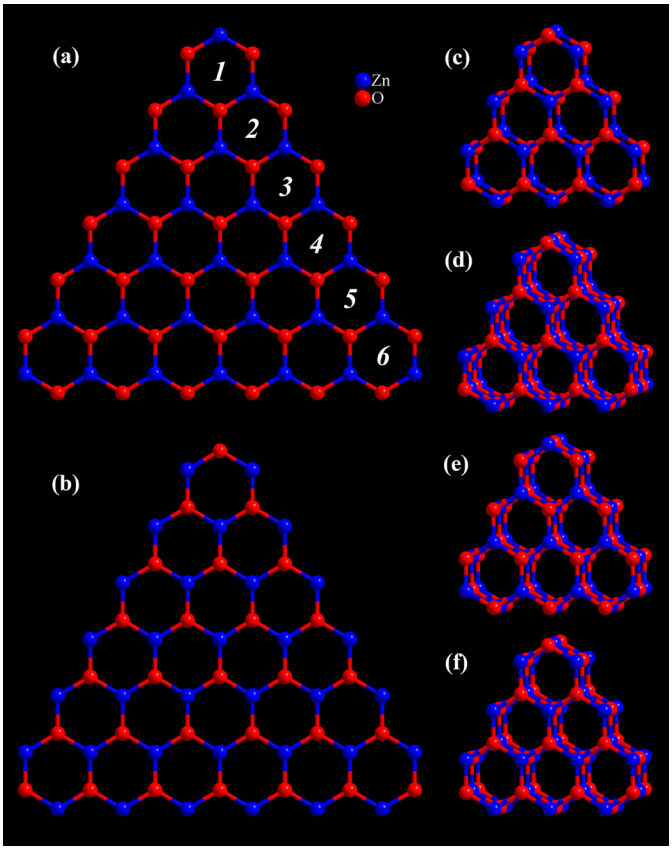

Fig. 1. Initial structures of monolayer ZnONIs: (a) O_6–ZnONI and (b) Zn_6–ZnONI. (c) Bi-layer and (d) four-layer ZnONIs, and tri-layer ZnONIs of (e) O–Zn–O and (f) Zn–O–Zn edges with size $n = 3$. Red and blue balls stand for O and Zn atoms.

Table 1
Average bond length B (Å) and formation energy E_f (eV/atom) of monolayer ZnONIs.

Size n	O_n–ZnONI			Zn_n–ZnONI		
	B_{edge}	B_{inner}	E_f	B_{edge}	B_{inner}	E_f
2	1.816	2.027	−0.613	1.836	2.047	−0.606
3	1.815	1.956	−0.707	1.865	1.940	−0.670
4	1.797	1.940	−0.776	1.859	1.942	−0.738
5	1.799	1.924	−0.849	1.866	1.932	−0.793
6	1.800	1.919	−0.872	1.864	1.929	−0.837
7	1.801	1.913	−0.907	1.862	1.926	−0.876

Owing to the dangling bonds of edge atoms, both types of nanoislands behave similar structural reconstructions with Zn (O) atoms near three corners inward (outward) motion, which is analogous to surface atoms relaxations in ZnO nanowires [34,35]. The optimized bond lengths are listed in Table 1. For both types of O_n–ZnONI and Zn_n–ZnONI, average bond lengths at three edges are much smaller than the corresponding ones at inner areas. This infers that Zn–O chemical bonds at the edges are much stronger than the inner ones. Especially for the chemical bonds near the corners, they are the strongest showing the smallest bond lengths. The average bond length at the edges varies irregularly with the increasing size, whereas the inner one gradually decreases and approaches to that of the monolayer ZnO sheet. All the bond lengths in ZnONIs deviate significantly from 2.0 Å in wurtzite ZnO bulk, exhibiting strong size effects.

To evaluate the structural stabilities of monolayer ZnONIs, the formation energy has been calculated according to the following formula

$$E_f = (E_{tot} - m\mu_O - n\mu_{Zn})/(m+n),$$