Structures and magnetic properties of ZnO nanoislands

Yu Yang1,2, Ping Zhang1*

1LCP, Institute of Applied Physics and Computational Mathematics, P.O. Box 8009, Beijing 100088, People’s Republic of China and
2Center for Advanced Study and Department of Physics, Tsinghua University, Beijing 100084, People’s Republic of China
(Dated: June 5, 2009)

Abstract

Using first-principles calculations, we systematically study the atomic structures and electronic properties for two dimensional triangular ZnO nanoislands that are graphite-like with monolayer and bilayer thickness. We find that the monolayer ZnO nanoisland with O terminated zigzag edges is magnetic at its ground state, with the magnetism coming from the O edge states. The other monolayer and bilayer ZnO nanoislands with different edge structures are all nonmagnetic at their ground states. It is further revealed that for different ZnO nanoislands, their magnetic properties are quite dependent on their sizes, with larger nanoislands having larger magnetic moments.

* Corresponding author. E-mail address: zhangping@iapcm.ac.cn
As a semiconducting metal oxide with a direct band gap, zinc oxide (ZnO) has vast applications in optoelectronics, transducers, and spintronics \[1, 2, 3\]. Recently, ZnO nanostructures of different morphologies have been fabricated and studied \[4, 5\]. Especially, graphite-like hexagonal ZnO nanofilms have been successfully fabricated \[6\] and extensively studied for possible usages in electronic devices \[7, 8, 9\]. Moreover, similar to the situations in graphene nanostructures, ZnO nanotubes and nanoribbons have then also been investigated for possible potential applications \[10, 11, 12, 13\]. It is noted that the monolayer ZnO nanoribbons with zigzag edges exhibit magnetic behavior \[13\]. Besides carbon nanotubes and graphene nanoribbons, two-dimensional (2D) graphene nanoislands have also been paid vast attentions because of their unique flexibility in tuning magnetic properties \[14, 15\]. Thus when turn to ZnO nanostructures, one may wonder whether 2D ZnO nanoislands show tunable magnetic properties or not. Especially when ZnO nanoisland samples is experimentally attainable by depositing hexagonal ZnO nanofilms on the Ag(111) surface \[6\]. Motivated by this question, in this paper we present systematical investigations on the atomic structures and electronic properties of 2D triangular ZnO nanoislands.

Moreover, the so-called $d^0$-magnetism have recently attracted extensive interests, which represents for magnetic behaviors in semiconducting materials (including ZnO) with the absence of transition metal doping. It was firstly observed in HfO$_2$ thin films where defects or oxygen vacancies cause magnetic behaviors \[16\]. Later, it has also been theoretically predicted that carbon doping in ZnO \[17\] and cation-vacancy in GaN and BN \[18\] both will lead to magnetic behaviors. In addition to these previous researches, here through first-principles calculations, we further reveal that the monolayer ZnO nanoisland with O terminated zigzag edge also shows magnetism in its ground state, even without any vacancies or defects.

In the present work, the first-principles calculations are carried out using the DMOL$^3$ package. Density functional semicore pseudopotentials (DSPP) \[19\] are adopted to replace the effects of core electrons of Zn and O with a simple potential including some degree of relativistic correction. The spin-polarized PW91 \[20\] functional based on generalized gradient approximation (GGA) is employed to take into account the exchange and correlation effects of electrons. For valence electrons, the double-numerical basis with polarized functions is adopted for expansion of the single-particle wave functions in Kohn-Sham equations. For better accuracy, the octupole expansion scheme is adopted for resolving the charge density.
and Coulombic potential, and a fine grid is chosen for numerical integration. The charge density is converged to \(1 \times 10^{-6}\) a.u. in the selfconsistent calculation. In the optimization process, the energy, energy gradient, and atomic displacement are converged to \(1 \times 10^{-5}\), \(1 \times 10^{-4}\) and \(1 \times 10^{-3}\) a.u., respectively. The atomic charge and magnetic moment are obtained by the Mulliken population analysis.

In the experiment by Tusche et al., the observed triangular 2D ZnO nanoislands all have the size of about 20 Å \(\text{Å}\). So we here start by investigating several kinds of ZnO nanoislands at this size, including the monolayer and bilayer ZnO nanoislands with both armchair and zigzag edges. It should be noted that there are two different kinds of zigzag edges (respectively the Zn- and O-terminated) for monolayer ZnO nanoislands. In total, five different ZnO nanoislands are studied here: the monolayer armchair-edge ZnO nanoisland (AZnONI), and zigzag-edge ZnO nanoisland with Zn- (Zn-ZZnONI) and O-terminated edges (O-ZZnONI), the bilayer armchair-edge (BAZnONI) and zigzag-edge ZnO nanoisland (BZZnONI). The optimized atomic structures for these ZnO nanoislands are all shown in Fig. 1.

During geometry optimizations, different kinds of ZnO nanoislands show different structural reconstructions. As shown in Figs. 1(a)-(c), after geometry optimizations for the monolayer ZnO nanoislands, all the atoms are still inside a same plane. For the AZnONI, the atoms at the edges and corners are distorted from their equilibrium places, and nine new Zn-Zn bonds form at the three edges as shown in Fig. 1(a). For the monolayer zigzag-edge ZnO nanoislands, the structural reconstructions only occur at the three corner areas. One can see from Fig. 1(b) that in the Zn-ZZnONI structure, the two Zn atoms at each corner come close with each other and form a new Zn-Zn bond, with the three O atoms at the corners pushed out from their original sites. In the O-ZZnONI structure shown in Fig. 1(c), the two O atoms at each corner move away from each other a little making the three Zn atoms at the corners pulled in from their original sites. The reconstructions for the BAZnONI and BZZnONI structures are more complex. Figures. 1(e) and (g) are respectively the side view for the atomic structures in the blue and red squares in Figs. 1(d) and (f), from which one can see that the atoms at corners and edges are no longer in the same plane with the middle atoms. The bond angles at these distorted areas are decreased to be smaller than 120°, indicating that these atoms incline to transit to the wurtzite configuration.

The electronic properties for the 2D ZnO nanoislands are then studied, and found to depend critically on their edge structures. Figure 2 shows the calculated energy levels for
the five geometrically optimized ZnO nanoislands with different edge structures. From Figs. 2(a), (d), and (e), we can clearly see that there exist large energy gaps for the A\text{ZnONI}, B\text{ZnONI} and B\text{ZZnONI} structures. This is in accordance with the saturation that the ratio between Zn and O atom numbers is 1:1 in them. The Zn-\text{ZZnONI} and O-\text{ZZnONI} structure respectively contains more Zn and O atoms, and thus are unsaturated. However, spin-splitting effect can only be observed for the O-\text{ZZnONI} structure as shown in Fig. 2(c). And the calculated total spin ($S_{\text{tot}}$) is 2. From the calculated energy levels shown in Fig. 2(c), we see that the energy difference between the highest occupied molecular orbital (HOMO) of spin-up and spin-down electrons ($E_{d} (\text{HOMO})$) is only 0.13 eV, which is very small and indicates that the spin-splitting effect is very weak. The smaller energy gap in individual gaps of spin-up and -down electronic states is defined as $E_{g}^{*}$, which is 0.18 eV and zero for the Zn- and O-\text{ZZnONI} structure respectively. The zero energy gap indicates that the O-\text{ZZnONI} structure is metallic at its ground state. And the small energy gap of 0.18 eV indicates that the Zn-\text{ZZnONI} structure is chemically not very stable. However, the Zn- and O-\text{ZZnONI} structures still might be fabricated using some special methods, since unpolarized hexagonal ZnO monolayers have been successfully produced already [6].

The deformation electron density and spin density are then further analyzed to study the origin of the magnetism in the O-\text{ZZnONI} structure. From the deformation electron density shown in Fig. 3(a), we can see that all the O atoms get some electrons from Zn atoms in the nanoisland. Mulliken charge density analysis further shows that the O atoms at the corners and edges get about 0.1 e more electrons than the O atoms in the middle of the nanoisland. These extra electrons might supply the excessive electrons in one spin state. Detailed wavefunction analysis proves that the electronic states around the Fermi energy are mainly contributed by the oxygen-dominated edge states. Figure 3(b) shows the spin density distribution in the O-\text{ZZnONI} structure. In this case, it is clear that the magnetic behavior is due to the oxygen edge states.

The fact that the O-\text{ZZnONI} structure without any magnetic impurities is magnetic might help us better understand the profound origin of magnetism in ZnO-based nanostructures. Besides, the magnetism in the O-\text{ZZnONI} structure also hints that it might has direct applications in nanoscale spintronics. So we further investigate the size effects on the magnetism in different O-\text{ZZnONI} structures, which can be differentiated by the number of O atoms at each edge ($i$), and we will use O$i$-\text{ZZnONI} to represent the O-\text{ZZnONI} structure of different
sizes. Based on this definition, the previously discussed O-ZZnONI structure is actually the O6-ZZnONI structure.

Table I shows the calculated magnetic and electronic properties for some O$i$-ZZnONI structures. We find that the value of all $E_d$ (HOMO) ranges between 0 and 0.2 eV, which is very small and indicates that the spin-splitting effect is weak for all the O$i$-ZZnONI structures. From the calculated $S_{\text{tot}}$ listed in Table I, we can see obvious quantum size effects. Except for O3-ZZnONI, the O$i$-ZZnONI structure with a larger size always has a larger total spin. From careful wavefunction analysis, we find that in the O3-ZZnONI structure, electrons of the middle oxygen atoms also contribute to its magnetic states. Considering that the magnetic states in other O$i$-ZZnONI structures are all contributed by their O edge states, this explains why the O3-ZZnONI structure has a larger $S_{\text{tot}}$ than the O4-ZZnONI and O5-ZZnONI structures. However, the abnormal large total spin of the O3-ZZnONI structure is because of its too small size. For most O$i$-ZZnONI structures, larger ones will have larger total spin.

In summary, we have systematically investigated the structures and magnetic properties for 2D ZnO nanoislands. It is found that the structural reconstructions are mainly around the three corners and three edges for triangular ZnO nanoislands. Among the five ZnO nanoislands with different edge structures, only the O-ZZnONI structure is magnetic at its ground state. And its spin density mainly distributes at the edge oxygen atoms. For the O-ZZnONI structure with different sizes, we reveal that the magnetic and electronic properties are quite dependent on their sizes. The O$i$-ZZnONI structure with a larger size always has a larger magnetic moment, implying their potential usages in spintronics.

This work was supported by the NSFC under grants No. 10604010 and No. 60776063.
[1] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen and T. Goto, Appl. Phys. Lett. 70, 2230 (1997).
[2] X. D. Bai, P. X. Gao and Z. L. Wang, Appl. Phys. Lett. 82, 4806 (2003).
[3] Z. L. Wang, X. Y. Kong, Y. Ding, P. Gao, W. L. Hughes, R. Yang and Y. Zhang, Adv. Funct. Mater. 14, 944 (2004).
[4] X. Y. Kong and Z. L. Wang, Nano Lett. 3, 1625 (2003).
[5] P. X. Gao, Y. Ding, W. J. Mai, W. L. Hughes, C. S. Lao and Z. L. Wang, Science 309, 1700 (2005).
[6] C. Tusche, H. L. Meyerheim and J. Kirschner, Phys. Rev. Lett. 99, 026102 (2007).
[7] C. L. Freeman, F. Claeyssens, N. L. Allan, and J. H. Harding, Phys. Rev. Lett. 96, 066102 (2006).
[8] J. Goniakowski, C. Noguera, and L. Giordano, Phys. Rev. Lett. 98, 205701 (2007).
[9] R. G. S. Pala and H. Metiu, J. Phys. Chem. C 111, 12715 (2007).
[10] B. L. Wang, S. Nagase, J. J. Zhao, and G. H. Wang, Nanotechnology 18, 345706 (2007).
[11] X. Shen, P. B. Allen, J. T. Muckerman, J. W. Davenport and J. C. Zheng, Nano Lett. 7, 2267 (2007).
[12] A. R. B. Médez, M. T. M. Martínez, F. L. Urías, M. Terrones and H. Terrones, Chem. Phys. Lett. 448, 258 (2007).
[13] A. R. B. Médez, F. L. Urías, M. Terrones and H. Terrones, Nano Lett. 8, 1562 (2007).
[14] J. F. Rossier and J. J. Palacios, Phys. Rev. Lett. 99, 177204 (2007).
[15] W. L. Wang, S. Meng and E. Kaxiras, Nano Lett. 8, 241 (2008).
[16] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature 430, 630 (2004).
[17] H. Pan, J. B. Yi, L. Shen, R. Q. Wu, J. H. Yang, J. Y. Lin, Y. P. Feng, J. Ding, L. H. Van, and J. H. Yin, Phys. Rev. Lett. 99, 127201 (2007).
[18] P. Dev, Y. Xue, and P. H. Zhang, Phys. Rev. Lett. 100, 117204 (2008).
[19] B. Delley, Phys. Rev. B 66, 155125 (2002).
[20] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
TABLE I: The energy difference of HOMO ($E_d$ (HOMO)), the smaller energy gap in individual gaps of spin-up and spin-down states ($E^*_g$), and the total spin ($S_{tot}$) for the Oi-ZZnONI structure with different sizes.

| $i$ | $E_d$ (HOMO) (eV) | $E^*_g$ (eV) | $S_{tot}$ |
|-----|-------------------|--------------|-----------|
| 3   | 0.01              | 0.19         | 2         |
| 4   | 0.08              | 0.06         | 1         |
| 5   | 0.17              | 0.06         | 1         |
| 6   | 0.13              | 0.00         | 2         |
| 7   | 0.04              | 0.02         | 3         |
List of captions

**Fig. 1**  (Color online). Atomic structures from top view for the AZnONI (a), Zn-ZZnONI (b), O-ZZnONI (c), BAznONI (d) and BZZnONI (f). (e) and (g) Atomic structures from side view for the selected atoms in (d) and (f). In all the structures, red and grey balls represent O and Zn atoms respectively.

**Fig. 2**  (Color online). Energy levels of AZnONI (a), Zn-ZZnONI (b), O-ZZnONI (c), BAznONI (d) and BZZnONI (e). The left and right columns in each figure correspond to spin-up and spin-down electronic states, respectively.

**Fig. 3**  (Color online). Contour plot of the deformation electron density (a) and isosurface plot of the spin density (b) for the O-ZZnONI. Red and grey balls respectively represent O and Zn atoms. The isosurface with the value of 0.01 $e/\text{Å}^3$ is shown in blue.
FIG. 1:
FIG. 2:
