Half-metallicity of wurtzite NiO and w-NiO/ZnO (0001) interface: First principles simulation

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(Received 9 January 2011; accepted 27 April 2011; published online 25 May 2011)

First principles calculations based on density functional theory (DFT) are performed to investigate the structural, electronic and magnetic properties of wurtzite NiO (w-NiO) and w-NiO/ZnO (0001) interface. By applying DFT+U method we discover that wurtzite NiO retains the half-metallic behavior in the w-NiO/ZnO (0001) heterostructure. Through analyses of density of state, charge population and magnetic moments, we find the half-metallicity is weakened around the interface but the interface effect is quite localized. More over the interface configuration keeps a ferromagnetic ground state as bulk w-NiO does. Based on the simulations of epitaxial growth case, w-NiO is predicted to be a promising candidate for electrode injecting spin polarized currents.

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I. INTRODUCTION

Injection of spin-polarized electrons - the key factor for achieving spintronics - has drawn great attention during recent decades. It is a popular way to use ferromagnetic (FM) metal as an injection source of spin-polarized electrons. However, one problem revealed is that the measured spin-polarization of current is rather weak, due to the conductivity mismatch between FM metals and semiconductors. So the search for substitute materials has been initiated to solve this obstacle, and until now many magnetic materials have been found. Among the substitute materials, some are discovered to have half-metallic property, which exhibits a metallic density of state (DOS) in one spin channel but a band gap around the Fermi energy (\(E_f\)) in the other. Thus the conduction electrons of half-metals that tunnel into semiconductors are 100% spin-polarized ideally, so half-metals are better spin injection sources than FM metals. So far, there have been many attempts to use half-metals, like Heusler alloys, as electrodes of spintronic devices, such as spin valves and tunneling magneto-resistive devices. Nevertheless, according to first principles calculations, the interface between half-metal and semiconductor will influence the electronic properties and in turn may destroy the spin polarization of the carriers.

Wurtzite NiO (w-NiO) has been predicted to display half-metallicity. Unlike conventional rocksalt NiO, w-NiO has been found to have only small lattice mismatch with some most popular wurtzite wide gap semiconductors such as ZnO, GaN, and SiC. Hence, epitaxial growth of w-NiO on these semiconductor substrates can be expected, even though wurtzite phase of NiO is metastable. Among these wide gap semiconductors, ZnO is the most promising candidate for the substrate material, since the w-NiO/ZnO (0001) interface consists of single element O that is shared by both ZnO and w-NiO, which will make such epitaxial growth coherent and successful. In addition, the interface O atomic monolayer makes Zn and Ni atoms separated and their interaction screened to some degree. So that this interface configuration may have a relatively slight effect on the electronic properties.

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properties and thus w-NiO will keep half-metallic at the interface, achieving injection of 100% spin-polarized electrons. However, neither experimental nor theoretical investigation of spin polarization of w-NiO/ZnO interface has been carried out so far.

In this paper, first-principles calculations have been performed on bulk w-NiO and w-NiO/ZnO (0001) interface based on density functional theory. Discussions of results have been focused on the structural, electronic and magnetic properties. We will show that w-NiO remains half-metallic at the interface against ZnO and it has promising applications in spintronics.

II. COMPUTATIONAL DETAILS

We employ the projector augmented wave (PAW)\textsuperscript{15} method in the framework of spin polarized density functional theory (DFT)\textsuperscript{16,17} as implemented in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{18} The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional\textsuperscript{19} is used in the calculation and the energy cut-off is 400 eV. The Brillouin zone is sampled using 4 × 4 × 5, and 6 × 6 × 2 Monkhorst-Pack grids\textsuperscript{20} for bulk and interface structures, respectively. Structure relaxation is performed using the conjugate gradient method\textsuperscript{21} and convergence criteria is that all forces are smaller than 0.02 eV/Å.

The w-NiO/ZnO (0001) interface is constructed applying (2 × 2 × 4) slab supercell containing 64 atoms, which consists of 8 w-NiO monolayers and 8 ZnO monolayers in a sequence of \ldots/\text{Ni}^{2+}/\text{Zn}^{2+}/\text{Ni}^{2+}0/\text{Zn}^{2+}/\ldots \ldots \text{the superscripts indicate the relative position of the monolayer along c axis; cf. FIG. 2(a)). There are two types of interfaces here as shown in FIG. 2(a) and both of them may exist experimentally. At interface I, the communal O\text{0} layer is closer to Ni\text{1} layer and one O\text{0} ion bonds with three Ni\text{1} neighbors and one Zn\text{1} neighbor. On the other hand, at interface II, each O\text{8} ion has one Ni\text{7} and three Zn\text{7} neighbors.

It should be noted that DFT gives inadequate description of the transition metal semicore 3d states, so the derived electronic properties deviate from the experimental results.\textsuperscript{22,23} For this reason, the DFT+U approach\textsuperscript{23} is adopted here, which introduces on-site Coulomb repulsion $U$ and exchange interaction $J$ on transition metal ions. Since dependence of w-NiO electronic structure on the magnitude of $U$ and $J$ has been discussed before,\textsuperscript{14} we simply adopt one set of proper values, $U = 4.5$ eV and $J = 0.5$ eV, that commonly used for Zn and Ni ions in previous publications.\textsuperscript{24,25}

III. RESULTS AND DISCUSSION

First the structural and electronic properties of bulk ZnO are examined and compared with other theoretical and experimental data. The relaxed lattice constants are $a = 0.321$ nm, $c = 0.516$ nm, which are in good agreement with experimental data of $a = 0.325$ nm, $c = 0.521$ nm.\textsuperscript{26} The spin resolved DOS is plotted in FIG. 1(a), and a band gap $E_g = 1.45$ eV is obtained which is similar to previous result of $E_g = 1.51$ eV with $U = 4.7$ eV.\textsuperscript{27}

Next we calculate the properties of bulk w-NiO. The fully relaxed lattice constants are $a = 0.308$ nm, $c = 0.539$ nm. Consistent with the discovery of Wu et al.,\textsuperscript{14} w-NiO only presents a band gap $E_g = 1.58$ eV in the spin up channel and the spin-flip gap is $E_{g}^{SF} = 1.26$ eV, which is defined as energy difference between $E_f$ and the conduction band minimum (CBM) in the semiconducting spin channel.\textsuperscript{14} The ground state of bulk w-NiO is found to be ferromagnetic with magnetic moment 1.67 $\mu_B$ of Ni and induced moment 0.28 $\mu_B$ of O. In comparison, we perform another calculation of w-NiO suffering a biaxial tensile strain, where the in-plane lattice constant $a$ is fixed to that of ZnO (0.321 nm), while the lattice constant $c$ and the atomic positions are fully relaxed. FIG. 1(b) displays the spin resolved DOS of this strained w-NiO. $E_f$ traverses the majority spin (up) energy gap but the minority spin (down) conduction band, clearly exhibiting half-metallic behavior. Compared to above fully relaxed case, the band gap $E_g = 1.14$ eV and the spin-flip gap $E_{g}^{SF} = 0.81$ eV become narrower. The ground state remains ferromagnetic with magnetic moments 1.64 $\mu_B$ of Ni and 0.32 $\mu_B$ of O.

To discover the interface effects on w-NiO in epitaxial growth situation, we perform calculations of w-NiO/ZnO (0001) interface configuration with fixed in-plane lattice constant $a = 0.321$ nm and investigate corresponding electronic and magnetic properties.
FIG. 1. (Color online) Spin resolved density of state of bulk ZnO (a) and bulk w-NiO with biaxial strain (b). The DOS is projected to each atom as denoted. In both (a) and (b) plots, the upper parts correspond to the spin up channel and vise versa. The Fermi energy is set to zero.

FIG. 2(b) displays the spin-resolved DOS that is projected to each ion in different monolayers of the interface configuration shown left. The uniform \( E_f \) remains in the energy gap of ZnO and the majority (spin up) gap of w-NiO, so that w-NiO preserves its half-metallicity at this epitaxial interface. Apart from this, the position of uniform \( E_f \) has changed in the energy gap compared to bulk materials (FIG. 1). It has moved upwards of 1.2 eV from the valence band maximum (VBM) of ZnO, but downwards slightly from the original position in the majority spin gap of bulk w-NiO. Accordingly, because of this \( E_f \) displacement and band overlap, the spin-flip gap has reduced to a narrower value \( E_{g}^{sp} = 0.24 \text{ eV} \) near the interface, and it has now become the difference between \( E_f \) and the CBM of ZnO (rather than w-NiO) in majority spin (up) channel. In spite of this \( E_f \) displacement, the w-NiO and ZnO parts of the heterostructure have their own energy gaps that have changed very slightly relative to bulk w-NiO (1.14 eV) and bulk ZnO (1.45 eV) respectively.

The interface influence on the electronic properties of both w-NiO and ZnO is localized, because the PDOS of all those inner ions (FIG. 2(b)) are similar to the PDOS of ions in corresponding bulk materials. For instance, like bulk ZnO (FIG. 1(a)), inner Zn\(^{3}\) or O\(^{-2}\), O\(^{-6}\) have almost symmetric PDOS regarding the two spins; and inner Ni\(^{3}\) or O\(^{6}\) show hybridization behavior beyond \( E_f \) in the minority spin (down) conduction band, which is also a characteristic of bulk w-NiO (FIG. 1(b)). On the other hand, ions near the two interfaces (shown in FIG. 2(a)) present the PDOS that are different from the PDOS of corresponding inner ions. At interfaceI, Ni\(^{1}\) or O\(^{0}\) have decreased minority spin PDOS around \( E_f \) exhibiting weaker half-metallicity than inner Ni\(^{3}\) or O\(^{2}\). Also, O\(^{0}\) is closer to w-NiO part, so its PDOS is more similar to the PDOS of O\(^{-2}\) than that of O\(^{-2}\), and Ni\(^{1}\) PDOS is more
affected than Zn$^{-1}$. In comparison, at interface II, Ni$^{7}$ is away from O$^{8}$ so its half-metallic property is as strong as the inner ones (Ni$^{3}$, Ni$^{5}$), while O$^{8}$ becomes totally insulate as O$^{6}$ in ZnO.

Evidence for the localization of interface effect can also be found from charge population of ions in each monolayer; cf. FIG. 3(a). Apart from interfacial ions, inner ones are less affected by the interfaces and all keep similar charge values to the counterpart ions in bulk material. At interface I, O$^{9}$ holds the intermediate charge value between the values of O at both sides; while at interface II, O$^{8}$ charge keeps the same value as the ones in ZnO. Ni charge decreases at both two interfaces, but Zn charge increases rather slightly. This charge transfer indicates that the interface ions denote electrons to construct the p-d bonds. For example, the p states of interfacial O$^{9}$ hybridize with neighboring Ni$^{7}$ d states and Zn$^{7}$ p, d states, contributing to the two minority spin PDOS peaks at around -2.1 eV and -3.2 eV; cf. FIG. 2(b).

FIG. 3(b) shows magnetic moments of ions in different monolayers in the interface configuration. Obvious changes of ionic magnetic moments are mainly around the interfaces: at interface I and II, O moments are between the values of inner O from ZnO and NiO; and Ni moments increase at the two interfaces. Nevertheless, inner O, Ni and all Zn keep almost the same magnetic moments as those ions of bulk materials, respectively. It is worthy to be noted that the difference between
magnetic moments of interfacial Ni$^1$ and inner Ni$^3$ is about 0.08 $\mu_B$, very close to the value of charge difference of $\sim 0.08$ e between corresponding Ni ions (FIG. 3(a)), which means electrons transfer from interfacial Ni and accordingly contribute to the increase of magnetic moments. Also we find that the majority spin (up) PDOS of interfacial Ni (Ni$^1$, Ni$^7$) have changed very little compared to inner ones (Ni$^3$) (FIG. 2(b)), so interfacial Ni electron transfer only occurs in the minority spin (down) channel. In contrast, between interfacial and inner O, differences of magnetic moments are a magnitude larger than differences of charges. This can be explained by the result of spin flip: for interfacial O, some minority (down) states originally around $E_f$ are pushed downwards to the valance band (FIG. 2(b)), and thus some O electrons flip from the spin up states to the spin down states of the same O ion, which makes interfacial O half-metallicity and magnetic moments decrease considerably but charge change slightly. All Ni, O, Zn have positive (parallel) magnetic moments,
indicating the ferromagnetic ground state of the interface system, in accordance with the \( w \)-NiO character.

In previous research of NiO/ZnO heterojunctions\(^{28-30} \), NiO all presented rocksalt structure with (111) lattice constants (∼ 0.296 nm) that were much smaller than ZnO (0001) lattice constant. However, according to our result above, wurtzite structure of NiO has a relatively small (0001) lattice mismatch (∼ 4.0\%) with ZnO. Therefore, \( w \)-NiO ultrathin film will possibly be fabricated by epitaxial growth, but no one has done this as far as we know. Recently, several experimental studies have been carried out focusing on spin polarization of the interface between magnetic materials and ZnO, such as Mg\(_2\)Zn\(_{1-x}\)O\(_x\)ZnO\(^{31} \), ZnMnO\(_x\)ZnO\(^{32,33} \), and CoO/ZnO\(^{34} \). Different methods of sample preparation and measurement of spin-dependent transport have been utilized in these experiments. Analogously, if \( w \)-NiO/ZnO heterostructure can be experimentally fabricated by these refined processes, the same methods can be utilized to investigate the spin polarization of \( w \)-NiO and to confirm whether the injection of spin-polarized electrons at \( w \)-NiO/ZnO (0001) interface is feasible.

### IV. CONCLUSION

Based on first principles calculations, we investigate the structural, electronic, and magnetic properties of bulk \( w \)-NiO and \( w \)-NiO/ZnO interface. It is found that the interface effects are highly localized and only make few changes to the properties of bulk ZnO and \( w \)-NiO materials. \( w \)-NiO remains its half-metallic property with 100\% spin polarization at \( E_f \). Suffering lattice strain and interface effect, the half-metallic property becomes slightly weak as the spin-flip gap decreases to 0.24 eV. Ground state magnetic configuration of the interface system keeps ferromagnetic as \( w \)-NiO does. As a consequence, efficient spin polarized electron injection is predicted to be possible at the \( w \)-NiO/ZnO (0001) interface, and this combination of \( w \)-NiO and ZnO has potential applications in spintronics.

### ACKNOWLEDGEMENTS

This research work is supported by the National High-tech R&D Program of China (863 Program) (Grant No. 2009AA01A402) and Innovative Foundation of Huazhong University of Science and Technology (Grant No. C2009Q007). Computational resources are provided by Wuhan National Laboratory for Optoelectronics (WNLO).

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