

RAPID COMMUNICATION

GaN/ZnO superlattice nanowires as photocatalyst for hydrogen generation: A first-principles study on electronic and magnetic properties

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Abstract

In hetero-nanostructures of solid state materials, the reconstruction of charge and spin at the interface can strongly affect the electronic and magnetic properties of the system. The nanomaterials with diverse functions can be achieved by precisely controlling the atomic structure and composition at the interface. Here, we present that the ferromagnetism and bandgap can be controlled by engineering the interfaces in non-magnetic semiconductor (GaN/ZnO) superlattice nanowires. We show that ferromagnetic p-type Zn-N interface can be developed by creating defects at the n-type Ga-O interface because of the defect-induced polar discontinuity. We further show that the bandgaps of the superlattice nanowires are narrowed with the formation of intermediate bands within the bandgaps, resulting in the enhancement of visible-light absorption. These nanostructures may find applications in photocatalyst for water splitting because of the improvement of carrier mobility and light absorption.

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Introduction

Finding sufficient supplies of clean energy for the future is one of society's most daunting challenges due to the limited supply of the old forms of depletable energy (coal, oil) and their detrimental effects on the global climate. Solar energy is considered to be the most important candidate because it is abundant, clean and renewable. The photo-electrochemical cell (PEC) splits water into hydrogen and oxygen, so as

to convert the solar energy into chemical energy, and has attracted increasing attention since the discovery of water splitting property of TiO₂ electrodes under ultraviolet (UV) illumination [1] due to the versatile applications of hydrogen and oxygen gases. However, the UV irradiation only accounts for ~5% of the solar spectrum and, as a consequence, the solar energy conversion efficiency of TiO₂ is limited due to its wide bandgap (~3.0 eV). Design of new photocatalysts is thus a critical step in solar energy harvesting. The development of efficient photocatalysts should satisfy: (1) an optimal band structure for maximal utilization of solar energy, (2) efficient photo-induced electron-hole separation and high carrier mobility, (3) large contacting

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surface area with the electrolyte, and (4) high stability in extreme environments [2–4]. Nanostructures show promising potency to enhance the solar energy harvesting by improving both light trapping, photo-carrier collection, and contacting surface area [5,6]. Semiconductor hetero-nanostructures, as important components of electronic and optoelectronic nanodevices, have attracted extensive attention [7–14]. By engineering the interfaces in the nano-heterostructures, nanodevices with versatile functions can be realized [7–14]. Recently, the concept, using the semiconductor hetero-nanostructures for solar energy conversion, has attracted considerable attention because the hetero-nanostructure could enhance the sun-light adsorption, carrier collection, and electron-hole separation, resulting in the improvement of the conversion efficiency with respect to the bulk-based solar cell [14–20]. Among the various hetero-nanostructures, the GaN/ZnO hetero-nanostructures should show particular and important application in solar energy conversion because of their similar electronic and structural properties. Both GaN and ZnO are direct wide bandgap semiconductors and have been used in optoelectronics. GaN is often used as the substrate for the growth of ZnO, and vice versa, because they have the same wurtzite crystal structure and lower lattice mismatch (1.8%) [21–25]. Recent development on the growth techniques, such as metalorganic vapor phase epitaxy (MOVPE) and facet-controlled epitaxial lateral overgrowth (FACELO), enables the growth of high quality of GaN/ZnO nanomaterials in a controlled manner [23–25]. Recently, the GaN/ZnO pseudobinary alloy was reported to be stable and has a higher efficiency for water splitting under visible light due to bandgap narrowing [26,27]. The mechanism of the bandgap narrowing has been intensely debated since the report of the alloy, such as *p-d* repulsion [28]. Wang et al. reported that the bandgap narrowing was attributed to the strong short-range order of GaN and ZnO in the alloy [29]. The incorporation of one compound into the other leads to the bandgap narrowing in the nonisovalent alloy, because ZnO and GaN have a type-II band alignment [29,30]. Most recently, Li et al. reported that the short-range order has significant influence over both structural and electronic properties [31]. Therefore, a fundamental study on the interface in the GaN/ZnO superlattice nanowires is crucial for our understanding of the bandgap-narrowing mechanism and the design of new photocatalyst with higher conversion efficiency. In this study, we present electronic structures of GaN/ZnO superlattice nanowires based on first-principles calculations. We find that the bandgaps of the GaN/ZnO superlattice nanowires are significantly reduced, leading to the visible-light absorption. We further show that the GaN/ZnO superlattice nanowires can be ferromagnetic by controlling the GaN/ZnO interfaces, which may improve the charge-separation of the photocatalyst.

Computational details

The first-principles calculation was carried out based on the density function theory (DFT) [32] and the Perdew-Burke-Eznerhof generalized gradient approximation (PBE-GGA) [33]. The projector augmented wave (PAW) scheme [34,35] as incorporated in the Vienna ab initio simulation package

(VASP) [36] was used. The Monkhorst and Pack scheme of *k* point sampling was used for integration over the first Brillouin zone [37]. The GGA+U method was used to treat 3d electrons of Ga and Zn. The Hubbard on-site Coulomb interaction parameter *U-J* was chosen to make the lattice constants of ZnO and GaN comparable with the experimental values. The interaction parameters of 2 eV and 6 eV for Ga and Zn, respectively, were used in the calculations. An energy cutoff of 500 eV was consistently used in our calculations. The grids for *k*-point sampling are $1 \times 1 \times 3$ for superlattice nanowires. Good convergence was obtained using these parameters, and the total energy was converged to 2.0×10^{-5} eV/atom. A large supercell dimension with a wall-to-wall distance of 10 Å in the plane perpendicular to the nanowire was used to avoid interaction between the 1-D nanostructure and its images in neighboring cells. The unit is periodic in the direction of superlattice nanowire axis along the [0001] of the wurtzite semiconductor.

Results and discussion

The bulk wurtzite GaN and ZnO were first optimized to get the lattice constants. The calculated lattice constants are $a=3.190$ Å and $c=5.185$ Å for GaN, and $a=3.215$ Å and $c=5.211$ Å for ZnO. The calculated bandgaps of bulk GaN and ZnO are 2.41 eV and 1.56 eV, respectively, which are lower than the experimental values due to the underestimation of DFT method, but consistent with the previous report [30]. Before studying the GaN/ZnO superlattice nanowires, we first calculated the GaN and ZnO nanowires (Supporting information, S-1) that comprised the superlattice nanowires studied in following. The bandgaps of the GaN and ZnO nanowires are 1.88 and 2.06 eV (S-1), respectively, which are larger than the reported values [38] because the GGA+U method was used in present study, but the band structures keep unchanged. The calculated partial density of states (PDOSs) of ZnO nanowire with unsaturated surface shows that the surface states do not apparently affect its band structure (S-2). Although the surface states of GaN nanowire with unsaturated surface contributes to the valence band top (S-3), they do not create additional defect bands within the bandgap (S-1 and S-3). The spin-polarized calculations show that the ZnO and GaN nanowires with unsaturated surfaces are non-magnetic. In our study of the GaN/ZnO superlattice nanowires, we focused on the effects of interfaces in the nanoscale on the electronic and magnetic properties, such as interface states within the bandgap and interface-induced ferromagnetism, and did not saturate the dangling bonds with hydrogen atoms on the surfaces to avoid the effect of H-saturation.

A GaN/ZnO superlattice nanowire is composed of two units of GaN and two units of ZnO nanowires ((GaN/GaN/ZnO/ZnO)_n) with hexagonal cross sections and has two interfaces, Ga-O and Zn-N interfaces (Fig. 1). At the Ga-O interface, one Ga atom (not at the edge) is bonded with three N and one O atoms (Fig. 1a). At the Zn-N interface, one Zn atom (not at the edge) is bonded with three O and one N atoms (Fig. 1a). To investigate the effects of the interfaces on the electronic and magnetic properties of the superlattice nanowires, various possible defects at the interfaces are considered. The defects at the Ga-O interface

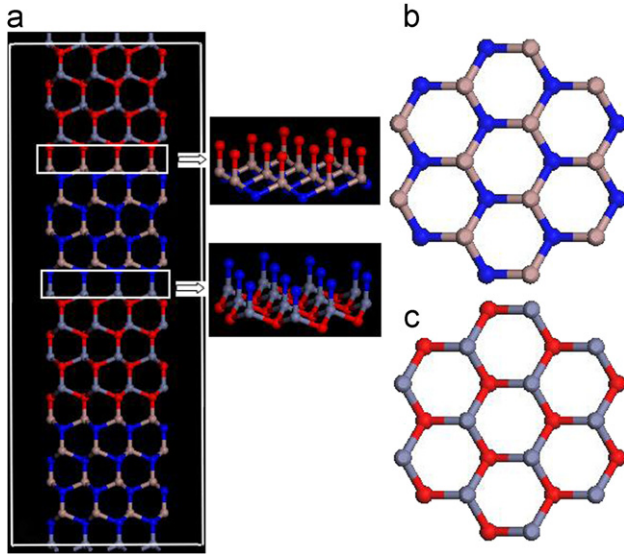


Fig. 1 The atomic configuration of GaN/ZnO superlattice nanowire (a) side view with fine views on the interfaces, (b) top view from GaN, and (c) top view from ZnO.

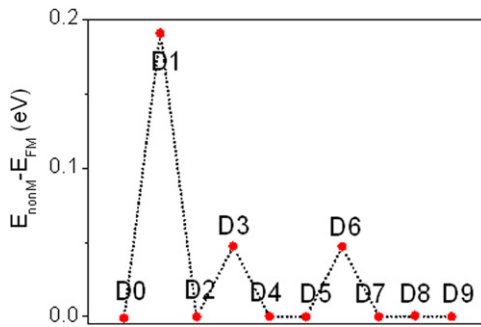


Fig. 2 The calculated energy difference between non-magnetic and magnetic states of GaN/ZnO superlattice nanowires without defect (D0) and with defects at the interfaces, including ZnN_{GaO} (D1), $ZnN_{GaO} + GaO_{ZnN}$ (D2), Zn_{Ga} (D3), O_N (D4), GaO_{ZnN} (D5), N_O (D6), Ga_{Zn} (D7), $N_O + O_N$ (D8), and $N_O + Ga_{Zn}$ (D9).

include N substitution of O (N_O), Zn substitution of Ga (Zn_{Ga}), and ZnN-pair substitution of GaO (ZnN_{GaO}). The defects at the Zn-N interface include O_N , Ga_{Zn} , and GaO_{ZnN} . We also studied the defect pairs at both of the interfaces, including $N_O + O_N$, $N_O + Ga_{Zn}$, and $ZnN_{GaO} + GaO_{ZnN}$.

The magnetic properties of the superlattice nanowires can be quantified by calculating the energy difference between the non-magnetic and magnetic states ($E_{nonM} - E_{FM}$). The superlattice nanowire without defect at the interfaces (D0) is non-magnetic because the energy of non-magnetic state is equal to that of magnetic state (Fig. 2). Similarly, the superlattice nanowires with defects (O_N , GaO_{ZnN} , and Ga_{Zn}) at the Zn-N interface (D4, D5, and D7) are non-magnetic. Interestingly, the superlattice nanowires with defects (ZnN_{GaO} , Zn_{Ga} , and N_O) at the Ga-O interface (D1, D3 and D6) are ferromagnetic. The $E_{nonM} - E_{FM}$ is about 47 meV for the superlattice nanowires with Zn_{Ga} and N_O , and about 190 meV for the superlattice nanowire with ZnN_{GaO} , indicating that the magnetic state can be improved by the pair

substitution at the Ga-O interface. However, if the number of defects at the two interfaces is equal, such as $ZnN_{GaO} + GaO_{ZnN}$, $N_O + O_N$, and $N_O + Ga_{Zn}$ (D2, D8 and D9), the superlattice nanowires are also non-magnetic. From the calculated $E_{nonM} - E_{FM}$, we find that the superlattice nanowire is ferromagnetic only if the number of defects at the Ga-O interface is larger than that at the Zn-N interface. To reveal the origin of the ferromagnetism, we investigate the electronic properties of the superlattice nanowire.

The calculated densities of states (DOSs) of the GaN/ZnO superlattice nanowire with defects at the Ga-O interface (ZnN_{GaO} , Zn_{Ga} , and N_O) clearly demonstrate their ferromagnetism (Fig. 3), as indicated by the asymmetrical spin-up and spin-down states near the Fermi level. The GaN/ZnO superlattice nanowire with ZnN_{GaO} (GaN/ZnO-D1) at the Ga-O interface is intrinsic semiconductor with a gap of about 1.65 eV in the spin-up structure, and p-type semiconductor with a gap of 1.42 eV in the spin-down structure (Fig. 3a), which are less than those of the corresponding GaN and ZnO nanowires (S-1) due to the type-II band alignment [29,30]. The holes in the spin-down structure are strongly spin-polarized, leading to its ferromagnetism. The analysis on the partial density of states (PDOSs) (Fig. 4) reveals that the spin-polarized states are dominated by the N_p electrons at the Zn-N interface (Fig. 4b). The calculated magnetic moment per N at the Zn-N interface is about 0.2 μ_B . We can also see that the localized defect states are within the bandgaps of both of the spin-up and spin-down states (at about 1 eV above the Fermi level), which may reduce the energy of photon to excite an electron from the valence band to conduction band. Similarly, the GaN/ZnO superlattice nanowires with Zn_{Ga} (GaN/ZnO-D3) and N_O (GaN/ZnO-D6) at the Ga-O interface are intrinsic semiconductors with the bandgaps of about 1.35 eV in the spin-up structure,

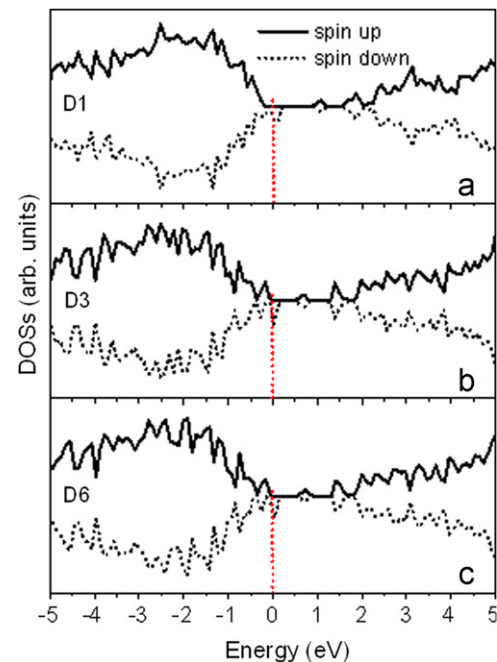


Fig. 3 The calculated densities of states (DOSs) of GaN/ZnO superlattice nanowires with defects at the Ga-O interface (a) ZnN_{GaO} (D1), (b) Zn_{Ga} (D3), and (c) N_O (D6).

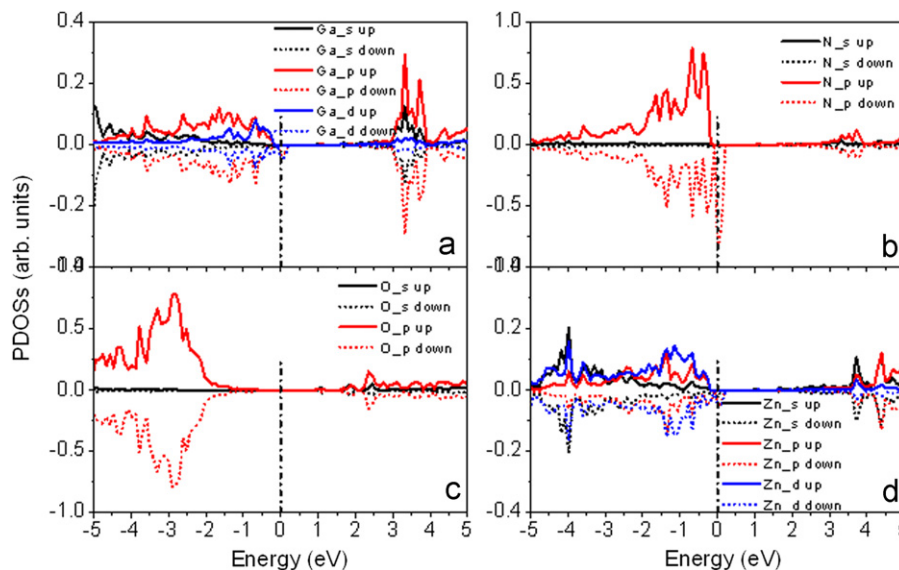


Fig. 4 The calculated partial density of states (PDOSs) of the GaN/ZnO superlattice nanowire with Zn_{GaO} (D1) at the Ga-O interface (a) Ga, (b) N, (c) O, and (d) Zn at the interfaces.

and p-type semiconductors with the bandgaps of about 1.25 eV in the spin-down structure (Fig. 3b and c). Their ferromagnetisms are attributed to the spin-polarized states in the spin-down structures, which are also dominated by the N_p electrons at the Zn-N interface. The calculated magnetic moments per N at the Zn-N interfaces of GaN/ZnO-D3 and GaN/ZnO-D6 are about $0.1 \mu_B$, which is half of the value of GaN/ZnO-D1. We predict that the defects in the Ga-O interface result in strong spin-polarization and enhance the magnetic moment, and the bandgaps of the superlattice nanowires are narrowed due to the type-II band alignment and the formation of defect bands within the bandgap. The narrowed bandgaps of the superlattices result in the enhancement of visible-light absorption. At the same time, the spin degeneracy of the bands in the ferromagnetic superlattices is lifted, and unwanted recombinations are impeded by spin selection rules or by low occupancy of states involved in the allowed recombinations [39,40]. The ferromagnetic superlattices thus provide more opportunities to improve the solar energy conversion efficiency due to the improved visible-light absorption, mobility, and charge-separation.

To understand the mechanism of the predicted GaN/ZnO interface magnetism, the comparison can be made to LaAlO₃-SrTiO₃ interface. The oxide hetero-interface introduces polar discontinuities, resulting in different electronic properties, such as insulating p-type (SrO)-(AlO₂)⁻ interface and conducting n-type (TiO₂)-(LaO)⁺ interface. [41,42] A ferromagnetic alignment of the induced electron spins within the n-type (TiO₂)-(LaO)⁺ interface had been theoretically predicted [43] and experimentally confirmed [44], where the magnetic moments arise from the polar discontinuity. GaN shows strong charge-polarization along [0001] direction [45]. N-terminated surface is positively charged, while Ga-terminated surface is negatively charged. For the GaN/ZnO superlattice nanowire, the Zn-N interface is p-type, and the Ga-O interface is n-type (Fig. 5a). Our first-principles calculation predicted that the p-type Zn-N interface is magnetic and the magnetic ordering is mainly

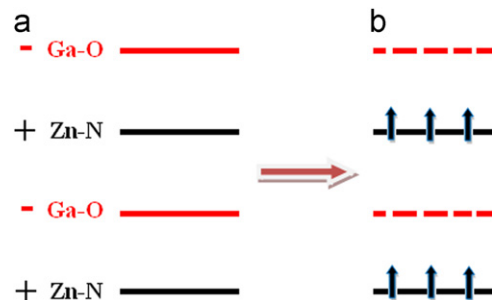


Fig. 5 The representative scheme for the charged interfaces in the superlattice nanowires. (a) Positive charged states at Zn-N interface is equal to those at the Ga-O interface, and (b) polar discontinuity. The dashed red lines show that the electrons at the n-type Ga-O interface are partially neutralized by p-type doping.

attributed to the N_p electrons at the Zn-N interface. Because the charged states at the n-type and p-type interfaces coexisted in GaN/ZnO superlattice nanowires without defects (D0), and with defects including Zn_{GaO} + Ga_{ZnN} (D2), N_O + O_N (D8) and N_O + Ga_{Zn} (D9) are equal (Fig. 5a), the polar discontinuities are not present, resulting in non-magnetic states (Fig. 2). The polar discontinuity can be artificially created by doping the n-type Ga-O interface with holes to partially neutralize the n-type charged states (Fig. 5b), *i.e.* Zn_{GaO} (D1), Zn_{Ga} (D3), or N_O (D6), which lead to spin-polarized states and ferromagnetism (Fig. 3). However, the polar discontinuity created by n-type doping at the p-type Zn-N interface, *i.e.* O_N, Ga_{ZnN}, or Ga_{Zn} (D4, D5 or D7), cannot result in the magnetic moment possibly due to charge disproportionation at the n-type Ga-O interface [43].

Although the GaN/ZnO superlattice nanowires without defect, with defects at Zn-N interface, or with same number defects at both of the two interfaces are not ferromagnetic, the narrowing of their bandgaps and the intermediate bands within their bandgaps (Fig. 6) should result in the improvement of the absorption of the sunlight as well as the

conversion efficiency. The GaN/ZnO superlattice nanowire (GaN/ZnO-D0) shows a semiconducting behavior with a bandgap of about 1.35 eV (Fig. 6a). Localized defect bands are observable in its bandgap, attributed to the localized

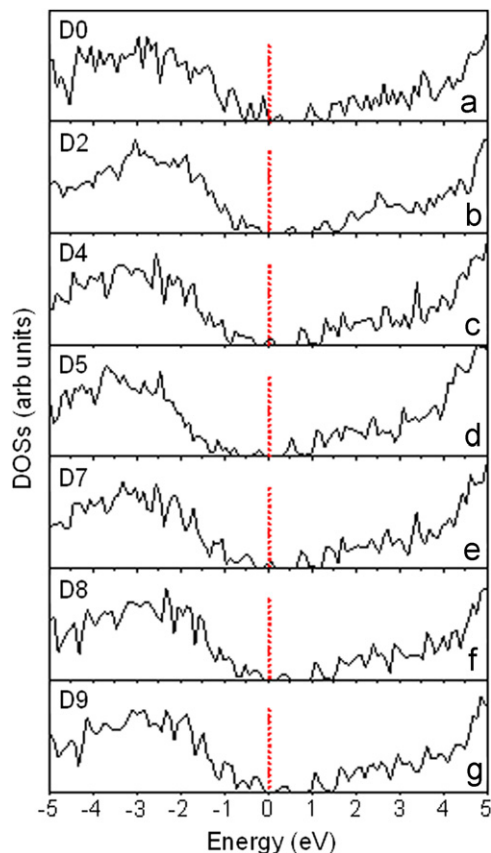


Fig. 6 The calculated densities of states (DOSs) of non-magnetic GaN/ZnO superlattice nanowires (a) without defect (D0), and with defects (b) $\text{ZnN}_{\text{GaO}} + \text{GaO}_{\text{ZnN}}$ (D2), (c) O_N (D4), (d) GaO_{ZnN} (D5), (e) Ga_{Zn} (D7), (f) $\text{N}_\text{O} + \text{O}_\text{N}$ (D8), and (g) $\text{N}_\text{O} + \text{Ga}_{\text{Zn}}$.

charge states at the interfaces. The calculated PDOSs show that these localized states near the top of valence band are mainly attributed to the N-p and Zn-d electrons in the Zn-N interface (Fig. 7b and d), and these below the bottom of conduction band are almost equally attributed to the electrons from the atoms at both of the interfaces (Fig. 7). Other non-magnetic GaN/ZnO superlattice nanowires also show semiconducting characters with narrowed bandgaps (Fig. 6b-g). Intermediate bands are observable within their bandgaps, which have the similar origin as those in GaN/ZnO-D0. The intermediate bands play an important role for the improved visible-light absorption of photocatalyst by reducing excitation energy [39,40] and would be one of the possible reasons for the visible-light photocatalytic activity of GaN/ZnO alloy [26].

Conclusion

Our first-principles calculations predicted that the ferromagnetism and bandgap narrowing can be achieved by engineering the interfaces in the polar semiconductor hetero-superlattice nanowires. We showed that the p-type Zn-N interface can exhibit ferromagnetic when the n-type Ga-O interface is doped with p-type elements, N, Zn, or both of them. The magnetic moments, dominated by the N_p electrons at Zn-N interface, are ferromagnetic alignment induced by the polar discontinuity. Our calculations further demonstrate that the bandgaps of ZnO/GaN superlattice nanowire are narrowed due to the traditional type-II alignment. The hetero-superlattice nanowires with controllable interfaces would be realized by various growth technologies, such as pulsed laser deposition (PLD), MOVPE, and FACELO, with artificially controlled growth conditions, such as modifying the O surface of ZnO before depositing GaN. Our findings open up the possibility for undoped all-semiconductor spintronics and may apply to the design for photocatalyst for water splitting based on the semiconductor hetero-nanostructures due to the bandgap narrowing

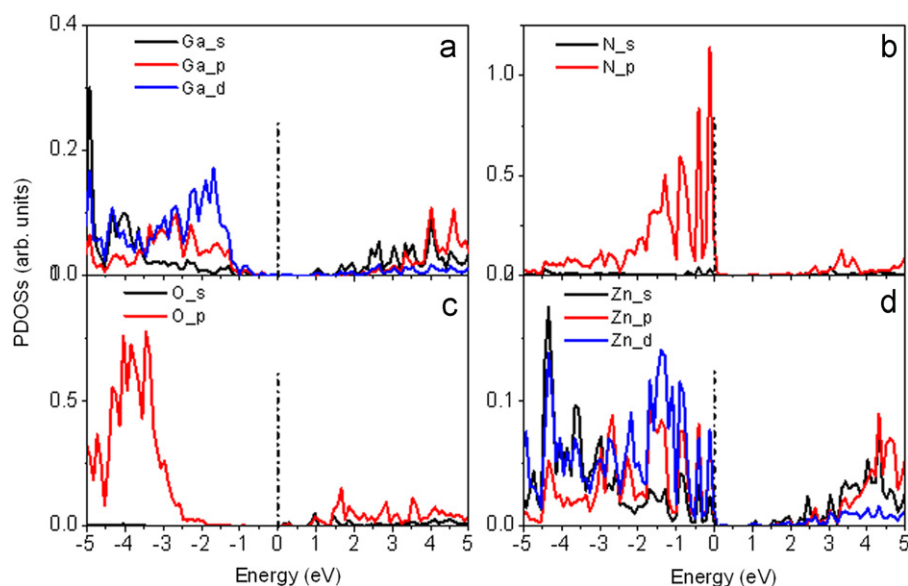


Fig. 7 The calculated partial density of states (PDOSs) of the GaN/ZnO superlattice nanowire without defect (D0) (a) Ga, (b) N, (c) O, and (d) Zn at the interfaces.

and improved charge-separation. The concept to obtain ferromagnetic semiconductors by creating polar discontinuity may be applicable for the design of novel materials with robust functions.

Acknowledgments

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Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at doi:[10.1016/j.nanoen.2012.03.001](https://doi.org/10.1016/j.nanoen.2012.03.001).

References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37–38.
- [2] X. Chen, S.S. Mao, *Chemical Reviews* 107 (2007) 2891–2959.
- [3] M. Gratzel, *Nature* 414 (2001) 338–344.
- [4] H. Pan, B. Guo, Z. Zhang, *Journal of Chemical Theory and Computation* 5 (2009) 3074–3078.
- [5] R. Yu, Q.F. Lin, S.F. Leung, Z.Y. Fan, *Nano Energy* 1 (2012) 57–72.
- [6] H. Pan, Y.W. Zhang, V. Shenoy, H.J. Gao, *ACS Catalysis* 1 (2011) 99–104.
- [7] L.J. Lauhon, M.S. Gudiksen, D. Wang, C.M. Lieber, *Nature* 420 (2002) 57–61.
- [8] G.S. Tseng, J.C. Ellenbogen, *Science* 294 (2001) 1293–1294.
- [9] R. Kapadia, Z.Y. Fan, K. Takei, A. Javey, *Nano Energy* 1 (2012) 132–144.
- [10] Z.R. Dai, J.L. Gole, J.D. Stout, Z.L. Wang, *Journal of Physical Chemistry B* 106 (2002) 1274–1279.
- [11] R. Yan, D. Gargas, P.D. Yang, *Nature Photonics* 3 (2009) 569–576.
- [12] M.S. Saha, R.Y. Li, M. Cai, X.L. Sun, *Journal of Power Sources* 85 (2008) 1079–1085.
- [13] H. Pan, C.K. Poh, Y. Zhu, G.C. Xing, K.C. Chin, Y.P. Feng, J. Lin, C.H. Sow, W. Ji, A.T.S. Wee, *Journal of Physical Chemistry C* 112 (2008) 11227–11230.
- [14] K. Wang, J.J. Chen, W.L. Zhou, Y. Zhang, Y.F. Yan, J. Pern, A. Mascarenhas, *Advanced Materials* 20 (2005) 3248–3253.
- [15] P. Nihan Kosku, T. Refik Sina, U. Emre, S. Mustafa Akin, T. Sumeyra, M. Evren, S. Ibrahim Murat, C. Huseyin, C. Gulsen, D. Hilmi Volkan, *Applied Catalysis B* 105 (2011) 75–85.
- [16] J.C. Lee, Y.M. Sung, T.G. Kim, H.J. Choi, *Applied Physics Letters* 91 (2007) 113104.
- [17] A. Srinivasan, O. Naoki, M. Masahiro, *Applied Catalysis B* 100 (2010) 502–509.
- [18] S. Kumar, M. Jones, S.S. Lo, G.D. Scholes, *Small* 3 (2007) 1633–1639.
- [19] B. Tian, X. Zheng, T.J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang, C.M. Lieber, *Nature* 449 (2007) 885–888.
- [20] Y. Zhang, L.W. Wang, A. Mascarenhas, *Nano Letters* 7 (2007) 1264–1269.
- [21] Y.I. Alivov, J.E. Van Nostrand, D.C. Look, M.V. Chukichev, D.M. Ataev, *Applied Physics Letters* 83 (2003) 2943–2945.
- [22] D.J. Rogers, F.H. Teherani, A. Yasan, K. Minder, P. Kung, M. Razeghi, *Applied Physics Letters* 88 (2006) 347–349.
- [23] H.L. Zhou, S.J. Chua, H. Pan, Y.W. Zhu, T. Osipowicz, W. Liu, K.Y. Zang, Y. Feng, C.H. Sow, *Journal of Physical Chemistry C* 111 (2007) 6405–6415.
- [24] T. Song, J.W. Choung, J.G. Park, W. Park, J.A. Rogers, U. Paik, *Advanced Materials* 20 (2008) 4464–4469.
- [25] H.L. Zhou, S.J. Chua, H. Pan, J.Y. Lin, Y.P. Feng, L.S. Wang, W. Liu, K.Y. Zang, S. Tripathy, *Electrochemical and Solid-State Letters* 10 (2007) H98–H100.
- [26] M. Yashima, K. Teramura, D.L. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, *Nature* 440 (2006) 295.
- [27] K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi, K. Domen, *Journal of the American Chemical Society* 127 (2005) 8286–8287.
- [28] L.L. Jensen, J. Muckerman, M.D. Newton, *Journal of Physical Chemistry C* 112 (2008) 3439–3446.
- [29] S. Wang, L.W. Wang, *Physical Review Letters* 104 (2010) 065501.
- [30] M.N. Huda, Y. Yan, S.-H. Wei, M.M. Al-Jassim, *Physical Review B* 78 (2008) 195204.
- [31] L. Li, J.T. Muckerman, M.S. Hybertsen, P.B. Allen, *Physical Review B* 83 (2011) 134202.
- [32] P. Hohenberg, W. Kohn, *Physical Review* 136 (1964) B864–B871.
- [33] J.P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters* 77 (1996) 3865–3868.
- [34] P.E. Blöchl, *Physical Review B* 50 (1994) 17953–17979.
- [35] G. Kresse, D. Joubert, *Physical Review B* 59 (1999) 1758–1775.
- [36] G. Kresse, J. Furthmüller, *Physical Review B* 54 (1996) 11169–11186.
- [37] H.J. Monkhorst, J. Pack, *Physical Review B* 13 (1976) 5188–5192.
- [38] H. Pan, Y.P. Feng, J. Lin, *ACS Nano* 2 (2008) 2410–2414.
- [39] P. Olsson, C. Domain, J.F. Guillemoles, *Physical Review Letters* 102 (2009) 227204.
- [40] H. Pan, Y.W. Zhang, V. Shenoy, H.J. Gao, *Applied Physics Letters* 96 (2010) 192510.
- [41] A. Ohtomo, H.Y. Hwang, *Nature* 427 (2004) 423–426.
- [42] N. Nakagawa, H.Y. Hwang, D.A. Muller, *Nature Materials* 5 (2006) 204–209.
- [43] R. Pentcheva, W.E. Pickett, *Physical Review B* 74 (2006) 035112.
- [44] A. Brinkman, M. Huijben, M. van Zalk, J. Huijben, U. Zeitler, J.C. Maan, W.G. van der Wiel, G. Rijnders, D.H.A. Blank, *Nature Materials* 6 (2007) 493–496.
- [45] J.S. Speck, S.F. Chichibu, *MRS Bulletin* 34 (2009) 304–309.



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