Origin of the Visible Light Absorption of GaN-Rich Ga$_{1-x}$ Zn$_x$N$_{1-x}$O$_x$ (x = 0.125) Solid Solution

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The structure, electronic, and optical properties of GaN-rich Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ (x = 0.125) solid solution have been investigated systemically by means of density functional theory calculations (DFT) within the generalized gradient approximation (GGA). Our calculated results indicate that between the N 2p and Zn 3d states there exists a strong p−d coupling, which results in a narrower band gap than that of GaN. According to our calculation, the narrowed band gap of the solid solution leads to the absorption of visible light and thus results in the photocatalytic activity under visible light. We also found that the position of the O atom has an obvious effect on the band gap of the solid solution. These results can give an explanation for the origin of the visible light activity of the solid solution and are in agreement with experimental observation.

1. Introduction

TiO$_2$ has been proven to be one of the most promising photocatalysts widely used in wastewater treatment and hydrogen generation.[1] However, pure bulk TiO$_2$ becomes active solely under ultraviolet light, which is only a small part (3−5%) of solar irradiation due to its wide band gap. Therefore, it is important to explore new photocatalysts that can be as a candidate for TiO$_2$. Recently, a new type of (oxy)nitride, the solid solution of GaN and ZnO with unique composition and structure containing d^{10} electronic configuration (Ga^{3+}), has been investigated as a photocatalyst for overall water splitting into H$_2$ and O$_2$ under visible light irradiation.[2−15] This solid solution represents the first successful example of overall water splitting using a photocatalyst with a band gap in the visible light region (<3 eV).[2] GaN has a band gap of about 3.4 eV, and its application in light-emitting diodes, laser diodes, and photocatalyst for overall water splitting under UV irradiation has been extensively reported.[16−20] ZnO with a band gap of about 3.2 eV also has been investigated, especially its applications in light-emitting diode and gas sensor aspects.[21,22] Because both materials have wurtzite structure with similar lattice parameters,[23,24] a solid solution of them can be formed and has been synthesized in experiment.[2,5] Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ solid solution has absorption edges in the visible light region and functions as a stable visible-light-driven photocatalyst for overall water splitting, which differs from GaN and ZnO only absorbing UV light due to their wide band gaps. In particular, when the solid solution loads appropriate cocatalysts such as RuO$_2$[2,5,6,8] and Rh−Cr mixed-oxide nanoparticles,[3,9,11] it shows reasonable photocatalytic activity for overall water splitting under visible light irradiation. However, there are few systemically theoretical studies about the electronic structure and the origin of photocatalytic activity under visible light of the Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ solid solution.[12] In ref 12, the effect of oxygen (zinc) concentration on the structural and electronic properties of Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ solid solution has been studied using DFT. To obtain a more detailed descrip-

tion about the structural and electronic properties of the solid solution with a certain oxygen (zinc) concentration, and to explore the relation between the electronic structure and the origin of photocatalytic activity under visible light irradiation, in this article, we investigated the geometric and electronic structure for the solid solution with oxygen (zinc) at different sites by means of DFT and explained the origin of the response to visible light of this solid solution.

In the Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$ solid solution, Zn and O atoms are regarded as substitutional atoms, respectively, for Ga and N atoms, and the substitution ratios of Zn to Ga and O to N are close to 1.[2,10,14] However, the positions of its constituent atoms are still unknown. In our study, a special quasirandom structure (SQS) approach,[25] which can be incorporated into different first-principle techniques easily, was employed to find favor configurations of the solid solution; special small-unit-cell periodic structures are constructed to closely model the most important structure features of the corresponding random solution. Thus, we simulated a 2 × 2 × 1 GaN supercell of the unit bulk cell with 16 atoms and then replaced a Ga atom with a Zn atom randomly. The substitution of an O atom to one N atom was performed at two kinds of site: first-nearest neighbors to the Zn atom and second-nearest neighbors to the Zn atom. The final stoichiometric proportion is Ga$_7$ZnN$_7$O (i.e., x = 0.125 in Ga$_{1-x}$Zn$_x$N$_{1-x}$O$_x$). To study the structure, electronic structure, and optical properties, we performed DFT calculations on these solid solution models. To study the individual effect of Zn or O atom on the electronic structure properties of GaN, we also performed DFT calculation on the substitutional one Zn atom to one Ga atom doped GaN and substitutional one O atom to one N atom doped GaN crystal models, respectively. All of these models are shown in Figure 1. Our theoretical calculations provide a reasonable explanation for the observation in experiment.

2. Calculation Details

The first principle calculations were performed by means of density functional theory (DFT) based on the plane wave pseudo potential[26] approach using the CASTEP package.[27] Exchange correlation potential was described by generalized

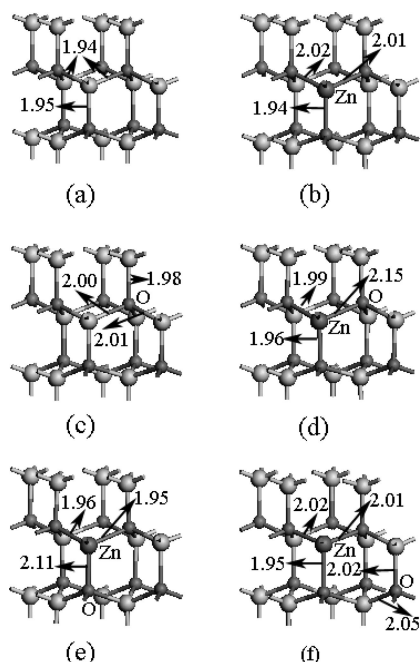* Corresponding author. E-mail: daiy60@sdu.edu.cn.

Figure 1. Models for (a) pure GaN structure, (b) one Zn atom substitutional to one Ga atom structure, (c) one O atom substitutional to an N atom structure, (d) one Zn atom substitutional to one Ga atom with one O atom at a first-nearest neighbor of Zn atom (above) structure, (e) one Zn atom substitutional to one Ga atom with one O atom at a first-nearest neighbor of Zn atom (below) structure, and (f) one Zn atom substitutional to one Ga atom with one O atom at a second-nearest neighbor of Zn atom structure. The light spheres represent Ga atoms; the gray spheres represent N atoms. Zn and O atoms are labeled. The unit of bond lengths is angstroms.

gradient approximation (GGA)[28] with the Perdew Burke Ernzerhof (PBE)[29] scheme. The interaction between valence electrons and ion core was substituted by ultrasoft pseudo potential.[30] Electronic wave functions were expanded in terms of a discrete plane wave basis set. The k space integrations were done with the Monkhorst−Pack[31] grid with $3 \times 3 \times 3$ k points in the Brillouin zone of the crystal to obtain the accurate density of the electronic states, and the kinetic energy cutoff for wave function expanding was 300 eV.

Geometry optimization was done before the single point energy calculation, and the self-consistent convergence accuracy was set at 5×10^{-5} eV/atom. The convergence criterion for the force between atoms was 0.1 eV/Å, the maximum displacement was 5×10^{-3} nm, and the stress was 0.2 Gpa. To check the reliability of our results, we also performed a calculation with a plane-wave cutoff energy of 340 eV for Ga_7ZnN_7O. As compared to the cutoff energy of 300 eV, little change of the results for both structural and electronic structures has been obtained, so that our calculated results in the present work are available. All of the electronic structures were calculated on the corresponding optimized crystal geometries.

3. Results and Discussion

3.1. Structure Relaxation and Formation Energies for Calculated Models. For pure GaN, the Ga−N bonds are 1.94 (three coordinates above Ga atom, one Ga−N bond is not shown in Figure 1a) and 1.95 Å (one below Ga atom). For the substitutional Zn to Ga doped GaN structure, Zn atom bonds to four adjacent N atoms (three above the Zn atom and one below the Zn atom). The bond lengths of the optimized Zn−N bonds are 2.01, 2.02, and 1.94 Å, respectively, which hardly have significant changes as compared to the original Ga−N bonds. Similar results are also obtained for the substitutional O to N doped GaN structure (see Figure 1c). When the O atom occupies the first-nearest neighbor site to the Zn atom in the solid solution structure, Zn−O bond is formed, and the bond length is 2.15 Å (see Figure 1d), slightly longer than the Ga−N bonds. Because the Zn−N bond above the Zn atom is slightly longer than the Zn−N bond below the Zn atom, we also calculated the substitutional O to N below the Zn atom doped structure (see Figure 1e). The optimized Zn−O bond length is 2.11 Å. When the O atom is at the second-nearest-neighbor site to Zn atom in the solid solution structure, the bond lengths of the optimized Zn−N, Ga−O bonds are shown in Figure 1f with no significant variation. These results indicate that the incorporation of Zn and O into the GaN lattice does not bring structure distortion and the formation of the solid solution is feasible.

To study the relative stability of the solid solution structure, we calculated the formation energies E_{form} for the five simulated
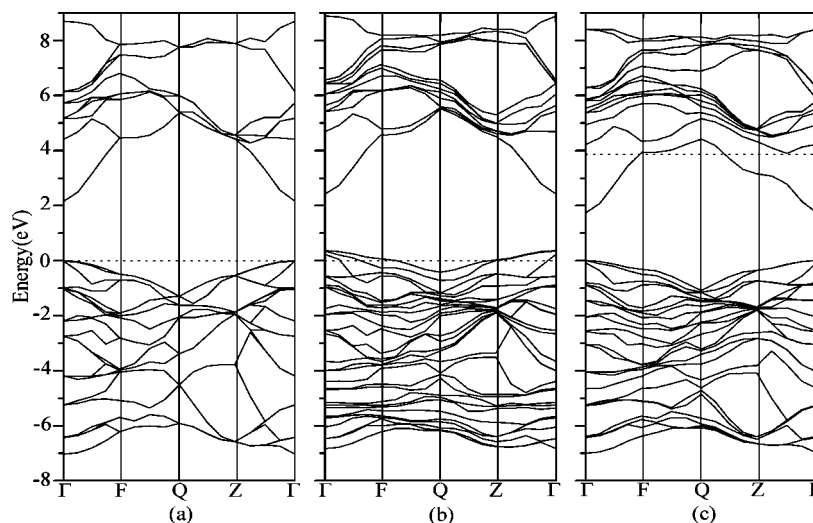

Figure 2. Band structures for models (a) bulk GaN, (b) one Zn atom substitutional to one Ga atom structure, and (c) one O atom substitutional to an N atom structure. The zero point is the top of the valence band in (c) and the highest occupied level in others. The dotted line represents the highest occupied level.

TABLE 1: Total Energies and Formation Energies for the Four Models Calculated (Unit Is eV)^a

models	Ga$_8$N$_8$	Ga$_7$ZnN$_8$	Ga$_8$N$_7$O	Ga$_7$ZnN$_7$O^1	Ga$_7$ZnN$_7$O^2	Ga$_7$ZnN$_7$O^3
E_{tot}	−18 664.13	−18 319.47	−18 829.38	−18 487.13	−18 487.01	−18 486.59
E_{form}		3.13	1.75	2.47	2.59	3.01

^{a} Ga$_7$ZnN$_7$O^1 represents the model for O substitute to N above Zn atom at a first-nearest neighbored site to the Zn atom; Ga$_7$ZnN$_7$O^2 represents the model for O substitute to N below Zn atom at a first-nearest neighbored site to the Zn atom; and Ga$_7$ZnN$_7$O^3 represents the model for O substitute to N at a second-nearest neighbored site to the Zn atom.
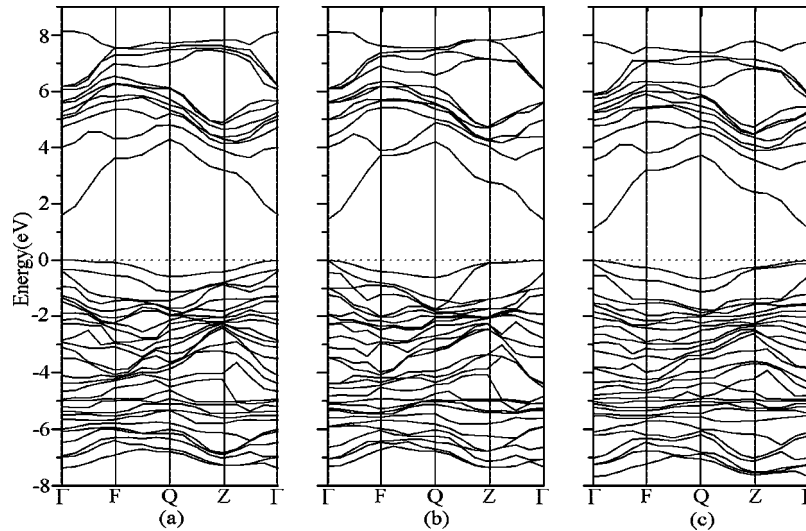

Figure 3. Band structures for models (a) O atom first-nearest neighbors to Zn atom (above) structure, (b) O atom first-nearest neighbors to Zn atom (below) structure, and (c) O atom second-nearest neighbors to Zn atom structure. The zero point represents the highest occupied level.

models, and the results are summarized in Table 1. The formation energies of the five models can be defined as follows,[32,33] respectively.

$$E_{form} = E_{tot}(\text{Ga}_7\text{ZnN}_8) - [E_{tot}(\text{GaN}) + \mu_{Zn} - \mu_{Ga}] \quad (1)$$

$$E_{form} = E_{tot}(\text{Ga}_8\text{N}_7\text{O}) - [E_{tot}(\text{GaN}) + \mu_O - \mu_N] \quad (2)$$

$$E_{form} = E_{tot}(\text{Ga}_7\text{ZnN}_7\text{O}) - [E_{tot}(\text{GaN}) + \mu_{Zn} + \mu_O - \mu_{Ga} - \mu_N] \quad (3)$$

where $E_{tot}(\text{Ga}_7\text{ZnN}_8)$, $E_{tot}(\text{Ga}_8\text{N}_7\text{O})$, and $E_{tot}(\text{Ga}_7\text{ZnN}_7\text{O})$ are the total energies of these three simulated models mentioned above, respectively. $E_{tot}(\text{GaN})$ is the total energy of the pure GaN supercell. The values of the chemical potential μ_O and μ_N are taken from the energy of N$_2$ and O$_2$ molecule. μ_{Zn} (μ_{Ga}) is the total energy per atom of bulk Zn (Ga). From Table 1 we can see that the formation energies are relatively small, indicating that the formation of the solid solution is easy. Our calculated results give smaller formation energies for the structures with the O atom at the first-nearest neighbored site to the Zn atom than the structure with the O atom at the second-nearest neighbored site to Zn atom, which indicates that the synthesis of the former structure is relatively easier. The almost equivalent total energies of the three solid solution structures illuminate that their relative stabilities are comparable.

3.2. Electronic Structure. First, we calculated the electronic structure of GaN supercell. The band structure is plotted in Figure 2a. We can see that GaN has a direct band gap of about 2.17 eV at the Γ point. Although the calculated band gap is underestimated as compared to the experimental value of about 3.4 eV due to the well-known limitation of the GGA approximation, the character of the band structure and the energy gap variations are expected to be reasonable and reliable. Figure 2b and c shows the band structures of the substitutional one Zn atom to one Ga atom doped GaN and substitutional one O atom

to one N atom doped GaN, respectively. According to Figure 2b, we can see that there are some unoccupied levels introduced above the highest occupied level without a significant change of the conduction band. These unoccupied levels can be considered to be acceptor levels with holes on them. In this situation, the crystal may have an intensity absorption in the long wavelength visible light region, resulting in the electronic transition from the filled valence band to the acceptor levels when the crystal is under irradiation. However, this has no contribution to the photocatalytic activity of the solid solution under visible light irradiation, as the energy of the photoactived electrons is not high enough to reduce H$^+$ to H$_2$. The substitution of O atom to an N atom introduces a donor level at the bottom of the conduction band (see Figure 2c), showing a typical n-type metallic character. Electrons transfer from the donor level to the unoccupied conduction band needs little photon transition energy, which results in the absorption of long wavelength visible light. In general, electrons on the donor level can transfer to the conduction band freely. When the crystal is under irradiation, electrons in the valence band transfer to the higher unoccupied conduction band above the donor level and need more photon transition energy. This results in an opposite effect on the photocatalytic activity for overall water splitting under visible light. The band structures of Ga$_7$ZnN$_7$O solid solution are shown in Figure 3. When the O atom takes up one N atom above the Zn atom at a first-nearest neighbor site to Zn atom, Figure 3a shows a band gap of about 1.6 eV that is narrower than the band gap of pure GaN. The narrowed band gap results in the reduction of photon transition energy for band gap excitation and thus is responsible for the photocatalytic activity under visible light of the solid solution. Comparing Figure 2b and c, the unoccupied acceptor levels shift below the highest occupied level; the unoccupied acceptor levels in Figure 2b change to be occupied in this situation, and the donor level
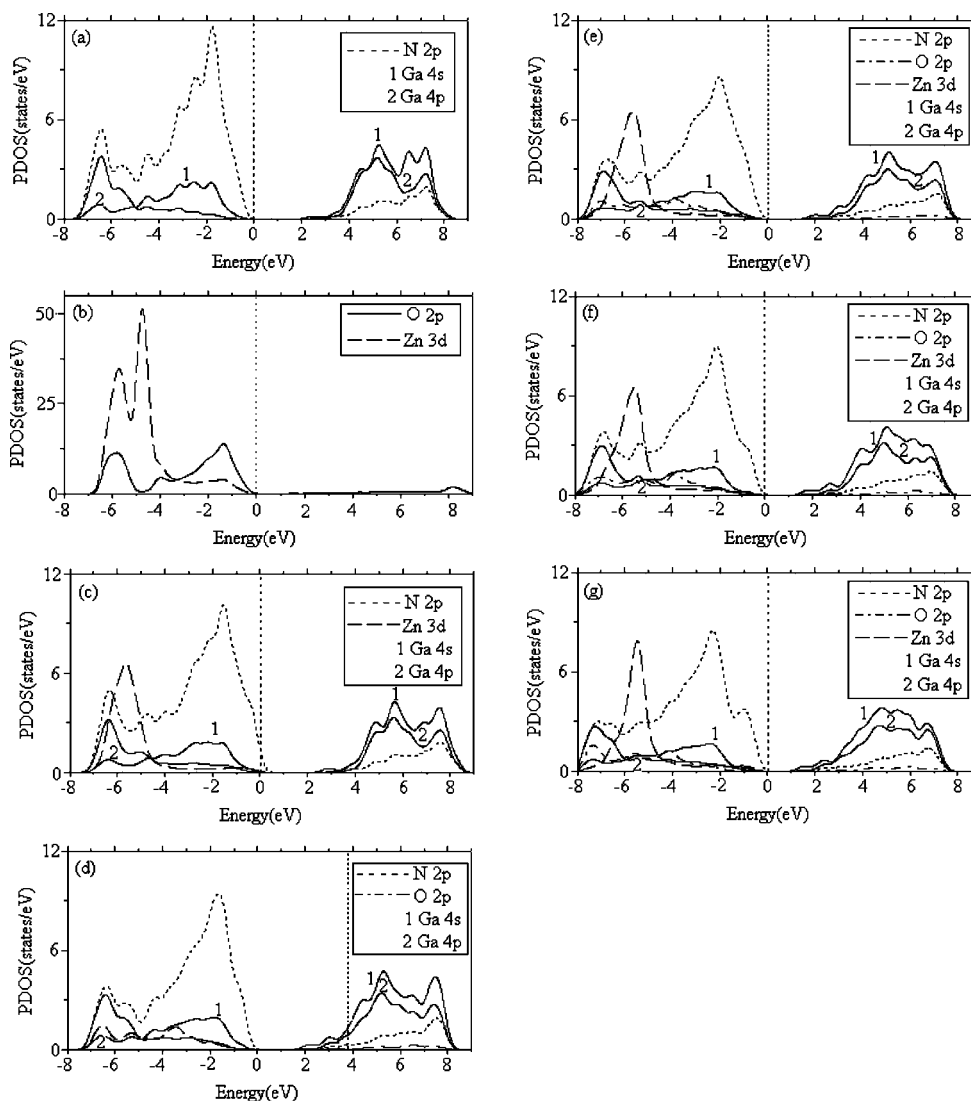
Figure 4. Projected density of states (PDOS) for (a) pure GaN structure, (b) pure ZnO structure, (c) one Zn atom substitutional to one Ga atom structure, (d) one O atom substitutional to an N atom structure, (e) one Zn atom substitutional to one Ga atom with one O atom at a first-nearest neighbor of Zn atom (above) structure, (f) one Zn atom substitutional to one Ga atom with one O atom at a first-nearest neighbor of Zn atom (below) structure, and (g) one Zn atom substitutional to one Ga atom with one O atom at a second-nearest neighbor of Zn atom structure. The zero point is the top of the valence band in (d) and the highest occupied level in others. The dotted line represents the highest occupied level.

changes to an empty band. This process in which electrons bound to donor level recombine with holes bound to acceptor levels is known as donor−acceptor pair (DAP) recombination.[34] The charge balance is kept by the introduction of Zn and O with the same number in the solid solution. When the O atom takes up the N atom below the Zn atom at a first-nearest neighbor site to Zn atom, Figure 3b indicates a similar result except for a further narrowed band gap of about 1.5 eV. When the O atom is at the second-nearest neighbored site to Zn atom, Figure 3c gives a band gap of about 1.1 eV. The differences between the band gaps may result from the effect of the variation of the local structure of these solid solution models. In summary, the narrowed band gap in visible light region is the indispensable factor for the photocatalytic activity of the solid solution of GaN and ZnO under visible light.

For a further analysis, we calculated the projected density of states (PDOS) and showed them in Figure 4. From the PDOS of pure GaN [see Figure 4a], we know that the conduction band primarily is constituted by Ga 4s and Ga 4p hybridized orbital and the upper valence band is formed by N 2p states from about −7.5 to 0 eV. Ga 3d states primarily centralize at −14.2 to

−12.7 eV [not shown in Figure 4a] in the valence band. To see the contribution of the Zn 3d and O 2p orbitals to the electronic structure, the PDOS of ZnO is also given in Figure 4b, in which we can see that Zn 3d orbitals mainly arrange from −6.8 to 0.0 eV in the deep valence band and O 2p orbitals distribute from −7.0 to 0.0 eV. For the substitution of a single Zn atom to a Ga atom in GaN, Figure 4c shows that the Zn 3d states shift downward a little as compared to that in ZnO and the N 2p states shift upward a little as compared to GaN, which indicates that there is a strong p−d repulsion between N 2p and Zn 3d states. This p−d repulsion raises the valence band maximum of Ga_7ZnN_8, which can be also understood as that the substitutional Zn atom exists as a Zn^{2+} ion at a Ga^{3+} site, releasing one less electron to the GaN lattice than does each Ga atom, so that there is an unoccupied state on the top of the valence band. For the case of substitutional one O atom to an N atom [corresponding to Figure 1c], the PDOS in Figure 4d shows that the O 2p orbitals shift slightly downward to an energy lower than that in ZnO; however, the bottom of the conduction band changes clearly due to the interaction between O atom and Ga atom. The highest occupied level is pinned at 3.88 eV

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in the conduction band, which means that the substitutional O atom exists at N site as an O^{2-} in GaN, and because the O^{2-} obtains one less electron from the GaN lattice than does each N atom, there are some occupied states at the bottom part of the conduction band. For Ga$_7$ZnN$_7$O with a first-nearest neighbored O atom to Zn atom [corresponding to Figure 1d and e], the PDOS are shown in Figure 4e and f. The presence of Zn 3d and N 2p states in the upper valence band of the solid solution provides p−d repulsion for the valence band maximum. Noticeably, the band widths of N 2p states are about 8.0 and 8.1 eV, respectively, which are wider than that in GaN of about 7.5 eV. A similar result is obtained from the O atom at a second-nearest neighbored site to Zn atom model [corresponding to Figure 1f] shown in Figure 4g. The bandwidth of the N 2p states about 8.5 eV confirms the broadened valence band.

4. Conclusion

GaN-rich GaN−ZnO solid solution has been studied by density functional theory calculation based on the plane wave method. To study the coeffect of Zn and O on the structural, electronic, and optical properties of the solid solution, we also calculated the substitutional Zn for Ga doped and substitutional O to N doped GaN structures, respectively. Our calculated results indicate that the substitution of Zn atom for Ga atom causes the formation of acceptor levels above the valence band and the substitution of O atom to N atom introduces donor level under the conduction band. The strong p−d repulsion between N 2p and Zn 3d states raises the valence band maximum in the GaN-rich Ga$_7$ZnN$_7$O solid solution, resulting in the narrowed band gap, which results in the reduction of photon transition energy. The relative position of the Zn atom and O atom also influences the band gap according to our calculation. Photocatalytic activity of the solid solution under visible light is attributable to the narrowed band gap.

References and Notes

(1) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735.

(2) Maeda, K.; Takata, T.; Hara, M.; Saito, N.; Inoue, Y.; Kobayashi, H.; Domen, K. *J. Am. Chem. Soc.* **2005**, *127*, 8286.

(3) Maeda, K.; Teramura, K.; Lu, D. L.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. *Nature* **2006**, *440*, 295.

(4) Waeda, K.; Domen, K. *J. Phys. Chem. C* **2007**, *111*, 7851.

(5) Maeda, K.; Teramura, K.; Takata, T.; Hara, M.; Saito, S.; Toda, K.; Inoue, Y.; Kobayashi, H.; Domen, K. *J. Phys. Chem. B* **2005**, *109*, 20504.

(6) Maeda, K.; Teramura, K.; Masuda, H.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. *J. Phys. Chem. B* **2006**, *110*, 13107.

(7) Maeda, K.; Teramura, K.; Lu, D.; Saito, N.; Inoue, Y.; Domen, K. *J. Phys. Chem. C* **2007**, *111*, 7554.

(8) Teramura, K.; Maeda, K.; Saito, T.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. *J. Phys. Chem. B* **2005**, *109*, 21915.

(9) Maeda, K.; Teramura, K.; Lu, D.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. *J. Phys. Chem. B* **2006**, *110*, 13753.

(10) Hirai, T.; Maeda, K.; Yoshida, M.; Kubota, J.; Ikeda, S.; Matsumura, M.; Domen, K. *J. Phys. Chem. C* **2007**, *111*, 18853.

(11) Maeda, K.; Hashiguchi, H.; Masuda, H.; Abe, R.; Domen, K. *J. Phys. Chem. C* **2008**, *112*, 3447.

(12) Jensen, L. L.; Muckerman, J. T.; Newton, M. D. *J. Phys. Chem. C* **2008**, *112*, 3439.

(13) Maeda, K.; Teramura, K.; Saito, N.; Inoue, Y.; Domen, K. *J. Catal.* **2006**, *243*, 303.

(14) Yashima, M.; Maeda, K.; Teramura, K.; Takata, T.; Domen, K. *Chem. Phys. Lett.* **2005**, *416*, 225.

(15) Maeda, K.; Teramura, K.; Domen, K. *J. Catal.* **2008**, *254*, 198.

(16) Nakamura, S.; Mukai, T.; Senoh, M. *Appl. Phys. Lett.* **1994**, *64*, 1687.

(17) Nakamura, S. *Science* **1998**, *281*, 956.

(18) Kocha, S. S.; Peterson, M. W.; Arent, D. J.; Redwing, J. M.; Tischler, M. A.; Turner, J. A. *J. Electrochem. Soc.* **1995**, *142*, L238.

(19) Huygens, I. M.; Strubbe, K.; Gomes, W. P. *J. Electrochem. Soc.* **2000**, *147*, 1797.

(20) Beach, J. D.; Collins, R. T.; Turner, J. A. *J. Electrochem. Soc.* **2003**, *150*, A899.

(21) Tsukazaki, A.; et al. *Nat. Mater.* **2005**, *4*, 42.

(22) Pizzini, S.; Butta, N.; Narducci, D.; Palladino, M. *J. Electrochem. Soc.* **1989**, *136*, 1945.

(23) Suhulz, H.; Thiemann, K. H. *Solid State Commun.* **1977**, *23*, 815.

(24) Garcia-Martinez, O.; Rojas, R. M.; Vila, E.; Martin de Vidales, J. L. *Solid State Ionics* **1997**, *63*, 442.

(25) Wei, S.-H.; Ferreira, L. G.; Bernard, J. E.; Zunger, A. *Phys. Rev. B* **1990**, *42*, 9622.

(26) Milman, V.; Winkler, B.; White, J. A.; Pickard, C. J.; Payne, M. C.; Akhmatskaya, E. V.; Nobes, R. H. *Int. J. Quantum Chem.* **2000**, *77*, 895.

(27) Segall, M. D.; Lindan, P. L. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C. *J. Phys.: Condens. Matter* **2002**, *14*, 2717.

(28) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(29) Perdew, J. P.; Bruke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(30) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.

(31) Monkorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188.

(32) Cui, X. Y.; Medvedeva, J. E.; Delley, B.; Freeman, A. J.; Newman, N.; Stampfl, C. *Phys. Rev. Lett.* **2005**, *95*, 256404.

(33) Valentin, C. D.; Pacchioni, G.; Selloni, A. *Chem. Mater.* **2005**, *17*, 6656.

(34) Bergman, P.; Ying, G.; Monemar, B.; Holtz, P. O. *J. Appl. Phys.* **1987**, *61*, 4589.