Oxygen vacancy in N-doped Cu_2O crystals: A density functional theory study*

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The N-doping effects on the electronic properties of Cu_2O crystals are investigated using density functional theory. The calculated results show that N-doped Cu_2O with or without oxygen vacancy exhibits different modifications of electronic band structure. In N anion-doped Cu_2O, some N 2p states overlap and mix with the O 2p valence band, leading to a slight narrowing of band gap compared with the undoped Cu_2O. However, it is found that the coexistence of both N impurity and oxygen vacancy contributes to band gap widening which may account for the experimentally observed optical band gap widening by N doping.

Keywords: oxygen vacancy, nitrogen, Cu_2O, first-principles

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1. Introduction

Cuprous oxide is a natively p-type semiconductor due to the presence of negatively charged copper vacancies and probably interstitial oxygen.[1−3] Cuprous oxide possesses a direct band gap of 2.17 eV, making it a good candidate for its applications in solar energy conversion and photocatalytic water splitting. It has also been used in catalysis, gas sensors, photovoltaic cells, lithium-ion batteries, and magnetic storages.[4−6] In addition, Cu_2O satisfies the economical and environmental requirement necessary for large scale application because it is an abundant, low-cost, and nontoxic material.[7] It is widely recognized that the electrical and photophysical properties of oxide materials are strongly influenced by electronic states associated with defects and dopants. Many attempts have been made to modify optical and electrical properties and transparency. A significant portion of these efforts relates to doping of Cu_2O with metal or nonmetal atoms. Therefore, the selection of suitable dopant atoms for Cu_2O is a key point. To date, the electronic properties of undoped as well as doped Cu_2O with impurities, both cations and anions, such as indium, cadmium, silicon, stannum, lanthanum, and chlorine have been investigated in order to realize the practical application of Cu_2O to solar cells and improve the transparency of Cu_2O using first principles calculations and experiment investigations.[8,9]

Nitrogen is widely accepted as a nontoxic, low-cost, and easily available material, and nitrogen doping of semiconductors is currently an active field of research both for efficient absorption of visible light by band gap modulation in photocatalysts (TiO_2, ZnO etc.) and for p-type conduction in light-emitting diodes (ZnO), other optoelectric devices (SnO_2) and solar cells (Cu_2O).[10−16] Ishizuka *et al.*[17] investigated the deposition conditions and dopant impurities and they found that nitrogen acted as a p-type dopant in Cu_2O with an activation energy of 140 meV and the hole density could be controlled. Recently, the synthesis of Cu_2O film doped with nitrogen (N) in which N substitutes for a lattice oxygen atom was reported in experiment.[18,19] Ishizuka *et al.*[18] found no significant band edge shift induced by N doping, while nitrogen acted as an acceptor in Cu_2O. However, Nakano *et al.*[19] observed the widened band gap of Cu_2O film by N doping. Nevertheless, the authentic origin has not been clarified in the doping scheme which was often the subject of debate.

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In the present work, the aim is to obtain the precise physical mechanism of N-doped Cu_2O. First-principles calculations based on the density functional theory are carried out to investigate the electronic structures of Cu_2O with nonmetal atom N-doping both with and without oxygen vacancy, which has never been reported by theoretical investigation.

2. Computation details

In the work, our calculated lattice constant for bulk Cu_2O is 4.30 Å (1 Å=0.1 nm), which is overestimated by only 0.7% with respect to the experiment value of 4.27 Å.[20,21] We simulate the N-doped Cu_2O system using a 2×2×3 (72 atoms) supercell. The results are shown in Fig. 1. The computation is performed by the CASTEP package on the basis of the density functional theory within the ultrasoft pesudopotential approach.[22] The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional based on the generalized gradient approximation (GGA) is employed.[23−26] The plane-wave basis convergence is found below 450 eV, and a Monkhorst–Pack k-point mesh of 4×4×4 is used for geometry optimization and electronic property calculation. Geometry optimization is carried out before single point energy calculation and the self-consistent convergence accuracy is set at 1.0×10^{-5} eV/atom. The convergence criterion of the largest force on atoms is 0.03 eV/Å and the maximal displacement is 1.0×10^{-4} nm. Electronic structures and total energies are calculated on the corresponding optimized crystal geometries.

3. Results and discussion

3.1. Model structures for oxygen vacancy in N-doped Cu_2O and relative stability

In principle, there are three possible ways to introduce N atoms into the Cu_2O lattice by replacing O or Cu atoms in the lattice with N atoms and introducing interstitial N atoms into the supercell. However, our calculations show that the formation energy of the model in which an N atom substitutes for an O atom is smallest. Therefore, the structure of O atoms replaced by N atoms and the role of oxygen vacancy are investigated in this work. Two combinations of N-doping and oxygen vacancy (V_O) are introduced, i.e., (i) one dopant and one oxygen vacancy (N_O+V_O), (ii) two dopants and one oxygen vacancy ($2N_O$+ V_O). For the N_O+V_O structure, the doping concentration maximum is up to 1.39 at%, the bond lengths between N and the four Cu atoms are equal to 1.818 Å, 1.818 Å, 1.812 Å, and 1.811 Å, which are shown in Fig. 1(b) (The Cu–O bond length is 1.864 Å in the structure of pure Cu_2O[21]). For the $2N_O$+V_O structure, the doping concentration maximum is up to 2.78 at%, the Cu–N bond lengths are 1.817 Å and 1.812 Å, respectively (see Fig. 1(c)). The structure of O atoms replaced by N atoms plus one oxygen vacancy does not result in obvious structural change compared with the structure of undoped Cu_2O and the structural modification is small with the increase of nitrogen concentration.

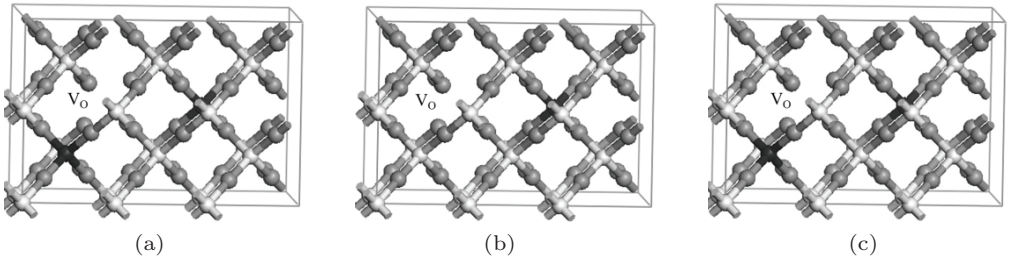


Fig. 1. Optimized structures of (a) 72-atom supercell, (b) N_O+V_O supercell, and (c) $2N_O$+V_O supercell. The white, gray, and black spheres denote O, Cu, and N atoms, respectively.

To study the variation of chemical bonding induced by N impurity with or without oxygen vacancy, the total charge densities for the three N-doped models are calculated and the results are shown in Fig. 2. Figure 2(a) presents the contour plot of charge density for (110) lattice plane of Cu_2O with an O atom replaced by an N atom, in which the N atom and adjacent Cu atoms form two coordinate bonds from a common electron cloud. For the model of substituting an N atom for an O atom plus an oxygen vacancy, the charge density map for the (110) lattice planes is calculated and the result is shown in Fig. 2(b). The

results show that the N atom and adjacent Cu atoms form N–Cu bonds by a common electron cloud and the charge distribution of the oxygen vacancy and neighbouring atoms appear to be different in comparison with the case of the N doping system due to the Cu atoms dangling bonds restructuring. Similar to the case of the model of substituting an N atom for an O atom plus an oxygen vacancy, the contour plot of charge density for $(1\bar{1}0)$ lattice plane of Cu_2O with two O atoms replaced by two N atoms plus one oxygen vacancy is also calculated and the result is shown in Fig. 2(c).

In order to examine the relative stability of different N-doped structures, we calculate the dopant formation energy according to the following equation:[27–29]

$$E_{\text{form}} = E_{\text{tot}}(N_{\text{O}}) - (E_{\text{pure}} + \mu_{\text{N}} - \mu_{\text{O}}), \quad (1)$$

$$E_{\text{form}} = E_{\text{tot}}(N_{\text{O}} + V_{\text{O}}) - (E_{\text{pure}} + \mu_{\text{N}} - 2\mu_{\text{O}}), \quad (2)$$

$$E_{\text{form}} = E_{\text{tot}}(2N_{\text{O}} + V_{\text{O}}) - (E_{\text{pure}} + 2\mu_{\text{N}} - 3\mu_{\text{O}}), \quad (3)$$

where E_{tot} is the total energy of Cu_2O with dopant, E_{pure} the total energy of the supercell of pure Cu_2O, and μ_{N} the chemical potential of N, which is determined by the energy of the N_2 molecule ($\mu_{\text{N}} = \mu(N_2)/2$). The growth of an engineered Cu_2O will not be an equilibrium process but a kinetic process, which can be either Cu-rich, O-rich, or anything in between. Under Cu-rich conditions, the μ_{Cu} chemical potential is assumed to be the energy of bulk Cu while the μ_{O} chemical potential is calculated by the growth condition,

$$\mu_{\text{O}} + 2\mu_{\text{Cu}} = \mu(Cu_2O). \quad (4)$$

Under O-rich conditions, the μ_{O} chemical potential is calculated from the ground-state energy of the O_2 molecule ($\mu_{\text{O}} = \mu(O_2)/2$), while the chemical potential of Cu is obtained by growth condition (4). The calculated formation energies are summarized in Table 1. Our calculations give smaller formation energies for one dopant and one oxygen vacancy model than those of two dopants and one oxygen vacancy under both Cu-rich and O-rich conditions, which indicates that the synthesis of the one dopant and one oxygen vacancy model may be relatively easy. Especially, the doped Cu_2O can be formed easily under Cu-rich growth conditions considering its formation energies.

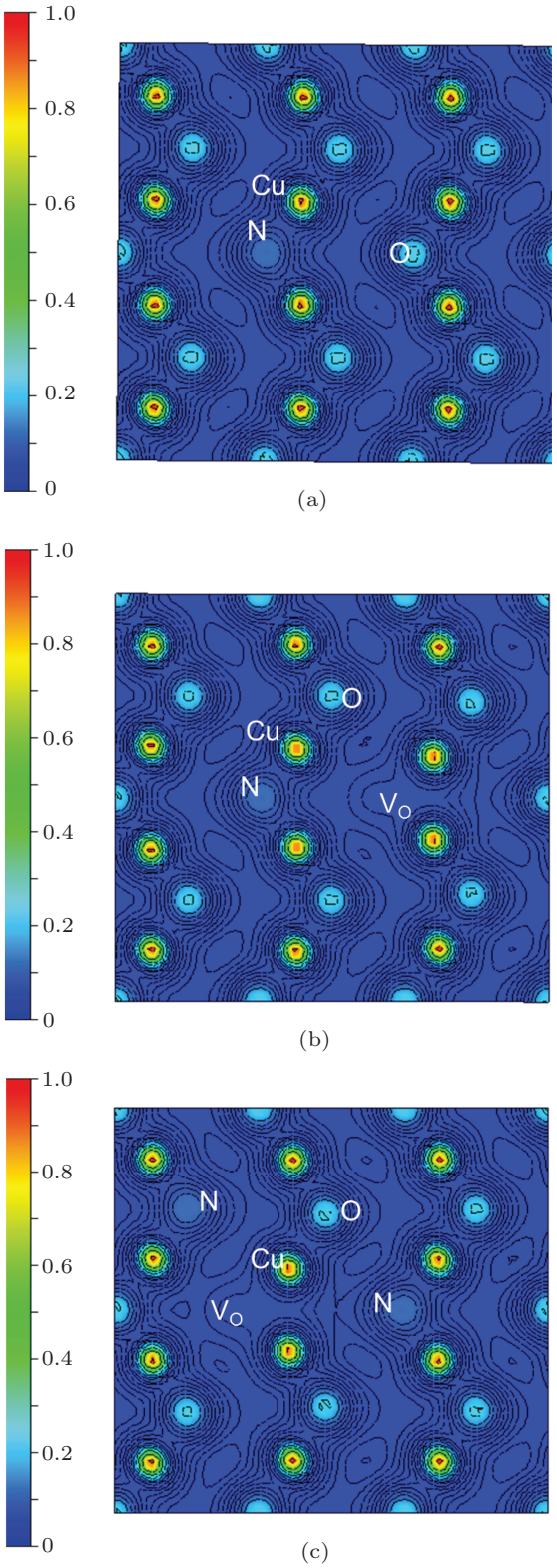


Fig. 2. (colour online) Total charge density maps (electrons/Å^3) of N-doped Cu_2O supercell with or without oxygen vacancy: (a) (110) lattice plane of Cu_2O with an O atom replaced by an N atom; (b) (110) lattice plane of Cu_2O with an O atom replaced by an N atom plus one oxygen vacancy; (c) $(1\bar{1}0)$ lattice plane of Cu_2O with two O atoms replaced by two N atoms plus one oxygen vacancy.

Table 1. The values of the lattice constant (Å) and the formation energy $E_{\rm form}$ (eV) of different kinds of N-doped structures.

Structure	$E_{\rm form}$(Cu-rich)	$E_{\rm form}$(O-rich)	a	c
Pure	–	–	8.61	12.91
N-doped	0.66	1.93	8.60	12.91
(N + V_O)-doped	1.26	3.78	8.54	12.85
(2N + V_O)-doped	1.79	5.57	8.53	12.84

3.2. Electronic structures

Cu_2O is a narrow gap semiconductor with a band gap in a range from 2 eV to 2.2 eV.[30−32] However, theoretical calculation on the electronic structure of the Cu_2O exhibits a small band gap ranging from 0.5 eV to 0.8 eV.[33−36] Our calculated band gap of pure Cu_2O at Γ point is about 0.53 eV. The well-established experimental value is typically significantly larger than the theoretical value. The reason is that the density functional theory method may usually underestimate the band gap because of the well-known problem in GGA approximation. However, it is still a widely accepted method to depict the defect states in the electronic structure calculation, and this gives an explanation for the experimental result because only the relative positions of the occupied states and empty states need to be taken into account.[12,37,38] To investigate the effects of N doping on the electronic and optical properties of Cu_2O, the band structure and the total density of states, and the projected density of the states of the N-doped 72 atom Cu_2O crystals are plotted in Fig. 3 and Fig. 4 respectively. For comparison, the band structure, the total density of states (TDOS) and partial density of states (PDOS) of the pure Cu_2O are also plotted. We can see that the valence band is mostly composed of O 2p states while the conduction band of Cu_2O is mainly composed of Cu 3d states, which is in agreement with previous studies.[36,39] For the model of substituting an N atom for an O atom, figure 4(a2) shows a small shift of valence band maximum towards higher energies because some N 2p states overlap and mix with the O 2p valence band, and thus increase the width of the valence band. Furthermore, there is a slight rise of the conduction band minimum, leading to band gap narrowing about 0.04 eV.

To examine the influence of the oxygen vacancy on the electronic structure of N-doped Cu_2O, one oxygen atom was removed from the N-doped Cu_2O system and the theoretical band structure and DOS were shown in Fig. 3(c) and Fig. 4(a3) respectively. For N_O+V_O model, the N 2p states overlap and mix with the O 2p valence band and the oxygen vacancy introduces some states close to the bottom of the conduction band which act as shallow donors. There is a slight rise of the valence band maximum compared with that of the undoped Cu_2O crystal while the conduction band minimum rises about 0.77 eV due to the formation of an oxygen vacancy, resulting in the band gap widening about 0.67 eV. The results show that the coexistence of both an N impurity and oxygen vacancy contributes to band gap widening. Therefore, N doping and the introduction of an oxygen vacancy have an obvious effect on the electronic structure. For the $2N_O$+ V_O model, some N 2p states mix with the O 2p valence band, leading to an increase of the width of the valence band as well as rises of about 0.13 eV and 0.81 eV for the valence band maximum and conduction band bottom, respectively, and thus, the band gap is widened by about 0.68 eV as shown in Fig. 3(d) and Fig. 4(a4) respectively. The calculation band gap is about 0.01 eV bigger for the replacement of two O atoms by N atoms plus one oxygen vacancy than that for the replacement of an O atom by an N atom plus one oxygen vacancy, which is due mainly to the change of the doping concentration. Our calculation for N anion-doped Cu_2O with an oxygen vacancy accounts for the experimentally observed widening of the optical band gap for P-type Cu_2O film by N doping.[19]

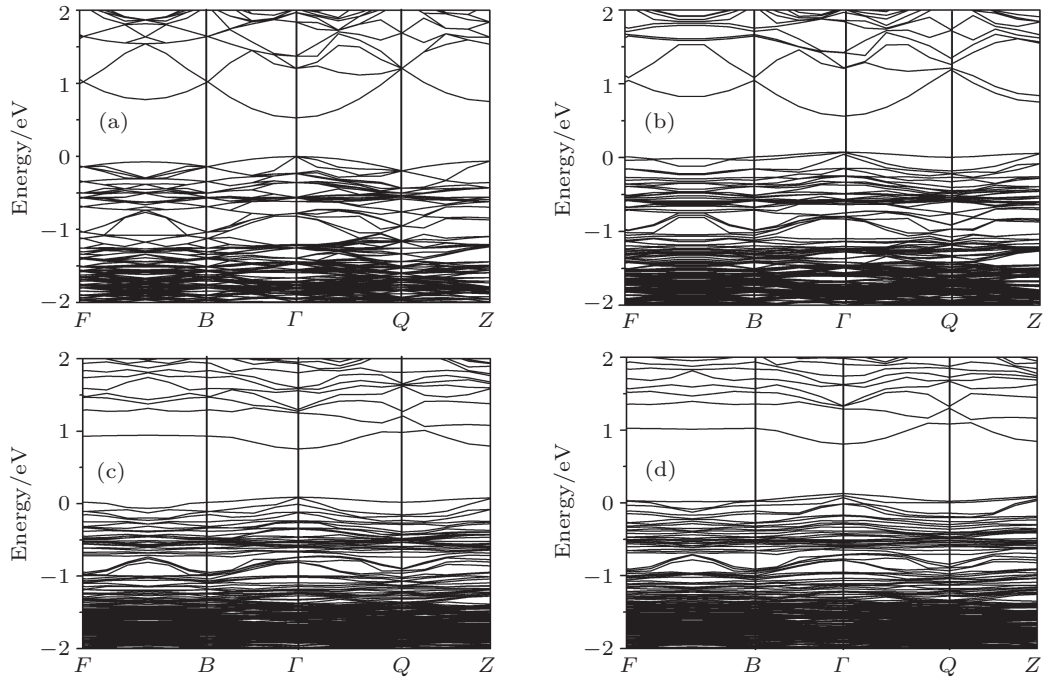


Fig. 3. Band structure plots for (a) pure Cu_2O, (b) substitution of an N atom for an O atom, (c) substitution of an N atom for an O atom plus one oxygen vacancy, and (d) substitution of two N atoms for two O atoms plus one oxygen vacancy, respectively.

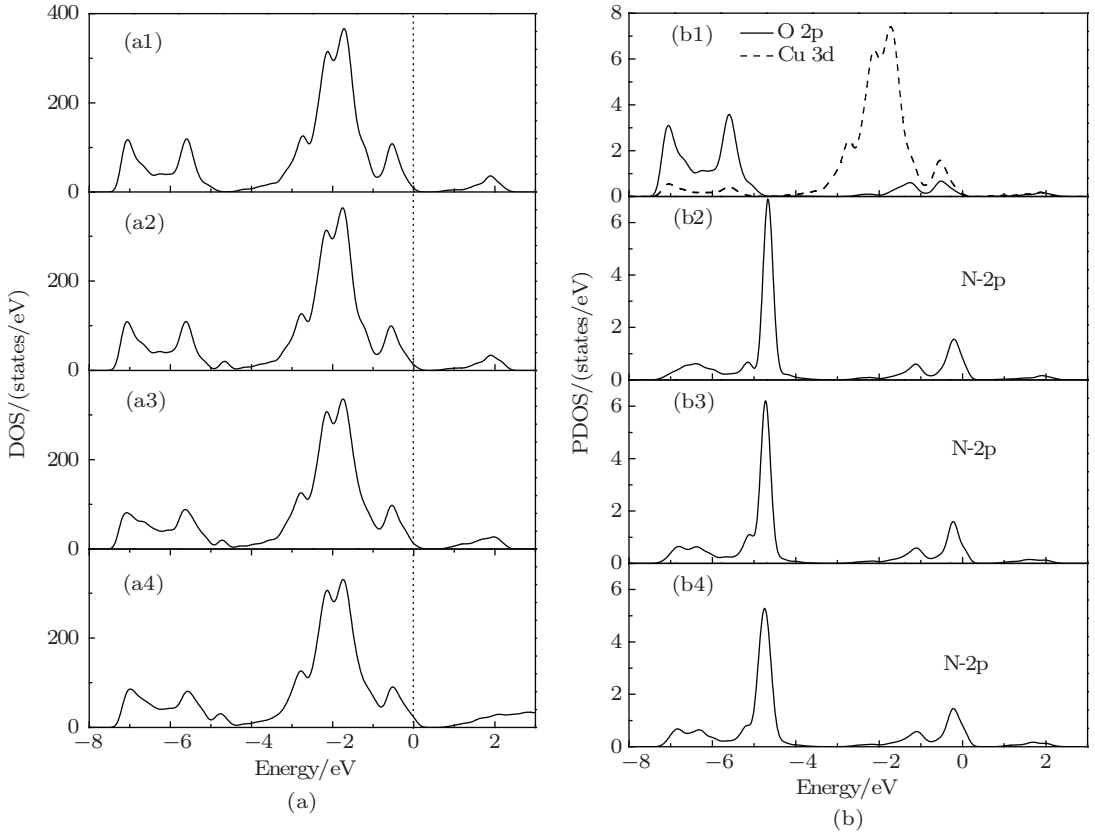


Fig. 4. (a) Total density of states (TDOS) and (b) projected density of states (PDOS) for 72-atom supercell: (a1) pure Cu_2O model and (a2) N_O model, (a3) N_O+ V_O model, (a4) $2N_O$+ V_O model, respectively. Zero energy is the Fermi level.

4. Conclusion

We investigated the electronic properties of N-doped Cu_2O with and without an oxygen vacancy using first-principles calculation. The calculated results indicate that different modifications of electronic band structure exist in N-doped Cu_2O with or without oxygen vacancy. It is shown that N impurities plus one oxygen vacancy in Cu_2O induce the widening of the band gap. In addition, some N 2p states mix with the valence band, leading to the increasing of the width of the valence band and there is a rather larger rise of the bottom of the conduction band which is due mainly to the formation of an oxygen vacancy. These results may account for the experimentally observed widening of the optical band gap by N doping.

References

[1] Grondahl L O 1933 *Rev. Mod. Phys.* **5** 141
[2] Porat O and Riess I 1995 *Solid State Ionics* **81** 529
[3] Nolan M and Elliott S D 2006 *Phys. Chem. Chem. Phys.* **8** 5350
[4] Poizot P, Laruelle S, Grugeon S, Dupront L and Taracon J M 2000 *Nature* **407** 496
[5] Briskman R N 1992 *Sol. Energy Mater. Sol. Cells* **27** 361
[6] Zhang J T, Liu J F, Peng Q, Wang X and Li Y D 2006 *Chem. Mater.* **18** 867
[7] Rai B P 1988 *Solar Cells: A Review. Sol. Cells* **25** 265
[8] Ishizuka S, Kato S, Okamoto Y and Akimoto K 2002 *Appl. Phys. Lett.* **80** 950
[9] Nolan M and Elliott S D 2006 *Phys. Chem. Chem. Phys.* **8** 5350
[10] Chen J, Jin G J and Ma Y Q 2009 *Acta Phys. Sin.* **58** 2702 (in Chinese)
[11] Zhang X J, Gao P and Liu Q J 2010 *Acta Phys. Sin.* **59** 4930 (in Chinese)
[12] Asahi R, Morikawa T, Ohwaki T, Aoki K and Taga Y 2001 *Science* **293** 269
[13] Nakano Y, Morikawa T, Ohwaki T and Taga Y 2005 *Appl. Phys. Lett.* **87** 232104
[14] Tsukazaki A, Ohtomo A, Onuma T, Ohtani M, Makino T, Sumiya M, Ohtani K, Chichibu S F, Fuke S, Segawa Y, Ohno H, Koinuma H and Kawasaki M 2005 *Nature Mater.* **4** 42
[15] Wei Y, Hu H F, Wang Z Y, Cheng C P, Chen N T and Xie N 2011 *Acta Phys. Sin.* **60** 027307 (in Chinese)
[16] Akimoto K, Ishizuka S, Yanagita M, Nawa Y, Paul G K and Saku-rai T 2006 *Sol. Energy* **80** 715
[17] Ishizuka S, Kato S, Okamoto Y, Sakurai T and Akimoto K 2002 *J. Cryst. Growth* **237** 616
[18] Ishizuka S, Kato S, Murayama T and Akimoto K 2001 *Jpn. J. Appl. Phys.* **40** 2765
[19] Nakano Y, Saeki S and Morikawa T 2009 *Appl. Phys. Lett.* **94** 022111
[20] Wickoff W G 1960 *Crystal Structures* Vol. 1 (New York: Wiley-Interscience)
[21] Werner A and Hocheimer H D 1982 *Phys. Rev.* B **25** 5929
[22] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[23] Perdew J P, Burke K and Ernzerhof M 1997 *Phys. Rev. Lett.* **78** 1396
[24] Perdew J P, Ruzsinszky A, Tao J, Staroverov V N, Scuseria G E and Csonka G I 2005 *J. Chem. Phys.* **123** 62201
[25] Perdew J P, Burke K and Wang Y 1996 *Phys. Rev.* B **54** 16533
[26] Milman V, Winkler B, White J A, Pickard C J and Payne M C 2000 *Int. J. Quantum Chem.* **77** 895
[27] Long R and English N J 2009 *Appl. Phys. Lett.* **94** 132102
[28] Ma X G, Wu Y, Lu Y H, Xu J, Wang Y J and Zhu Y F 2011 *J. Phys. Chem.* C **115** 16963
[29] Wang P, Liu Z R, Lin F, Zhou G, Wu J, Duan W H, Gu B L and Zhang S B 2010 *Phys. Rev.* B **82** 193103
[30] Baumeister P W 1961 *Phys. Rev.* **121** 359
[31] Ghijsen J, Tjeng L H, van Elp J, Eskes H, Westerink J, Sawatsky G A and Czyzyk M T 1988 *Phys. Rev.* B **38** 11322
[32] Ghijsen J, Tjeng L H, Eskes H, Sawatsky G A and Johnson R L 1990 *Phys. Rev.* B **42** 2268
[33] Soon A, Todorova M, Delley B and Stampfl C 2007 *Phys. Rev.* B **75** 125420
[34] Martínez-Ruiz A, Moreno M G and Takeuchi N 2003 *Solid State Sci.* **5** 291
[35] Ching W Y, Xu Y N and Wong K W 1989 *Phys. Rev.* B **40** 7684
[36] Soon A, Todorova M, Delley B and Stampfl C 2006 *Phys. Rev.* B **73** 165424
[37] DiValentin C, Pacchioni G, Selloni A, Livraghi S and Giamello E 2005 *J. Phys. Chem.* B **109** 11414
[38] Lee J, Park J and Cho J 2005 *Appl. Phys. Lett.* **87** 011904
[39] Soon A, Sohnel T and Idriss H 2005 *Surf. Sci.* **579** 131