Comparative study of adsorption characteristics of Cs on the GaN (0001) and GaN (000$\bar{1}$) surfaces*

Du Yu-Jie(杜玉杰)[a)b)], Chang Ben-Kang(常本康)[a)†], Wang Hong-Gang(王洪刚)[a)], Zhang Jun-Ju(张俊举)[a)], and Wang Mei-Shan(王美山)[c)]

[a)] *Department of Physics and Electronic Sciences, Institute of Bingzhou, Bingzhou* 256603, *China*

[b)] *Institute of Electronic Engineering and Opto-Electric Technology, Nanjing University of Science and Technology, Nanjing* 210094, *China*

[c)] *School of Physics and Optoelectronic Engineering, Ludong University, Yantai* 264025, *China*

(Received 28 January 2012; revised manuscript received 28 February 2012)

The adsorption characteristics of Cs on GaN (0001) and GaN (000$\bar{1}$) surfaces with a coverage from 1/4 to 1 monolayer have been investigated using the density functional theory with a plane-wave ultrasoft pseudopotential method based on first-principles calculations. The results show that the most stable position of the Cs adatom on the GaN (0001) surface is at the N-bridge site for 1/4 monolayer coverage. As the coverage of Cs atoms at the N-bridge site is increased, the adsorption energy reduces. As the Cs atoms achieve saturation, the adsorption is no longer stable when the coverage is 3/4 monolayer. The work function achieves its minimum value when the Cs adatom coverage is 2/4 monolayer, and then rises with Cs atomic coverage. The most stable position of Cs adatoms on the GaN (000$\bar{1}$) surface is at H3 site for 1/4 monolayer coverage. As the Cs atomic coverage at H3 site is increased, the adsorption energy reduces, and the adsorption is still stable when the Cs adatom coverage is 1 monolayer. The work function reduces persistently, and does not rise with the increase of Cs coverage.

Keywords: GaN surface, electronic structure, adsorption energy, work function

PACS: 71.55.Eq, 78.20.Ci **DOI:** 10.1088/1674-1056/21/6/067103

1. Introduction

GaN is commonly used as a new semiconductor material for its fascinating properties, such as a wide band gap, high thermal conductivity, high breakdown voltage, high melting point and chemical stability, among others.[1,2] GaN has promising applications in the field of electronic devices,[3−5] such as in high-temperature devices, high-power devices, and the optoelectronic devices field such as blue light-emitting diodes (LEDs),[6,7] blue lasers (LDs)[8,9] and ultraviolet detectors.[10,11] Negative electron affinity (NEA) can be obtained by reducing the work function of the GaN (0001) surface covered by Cs and O, which has been studied experimentally.[12−14] The GaN ultraviolet photocathode based on NEA is a very good cold electron source, and has important application value in flat electronic printing and vacuum ultraviolet detection.[15−17] For the difference between surface properties of GaN (0001) and (000$\bar{1}$) surfaces,[18] the adsorption characteristics of Cs on GaN (0001) and GaN (000$\bar{1}$) surfaces may have differences which have been rarely studied. The electronic structure and optical properties of the GaN (0001) surface adsorbed by a single Cs atom have been investigated by us using the density functional theory with a plane-wave ultrasoft pseudopotential method based on first-principles calculations.[19] Based on this study, the influence of Cs coverage on adsorption energies and the work function of GaN (0001) and (000$\bar{1}$) surfaces have been studied further, and the differences as well as the reasons between the surface adsorption characteristics of Cs on GaN (0001) and (000$\bar{1}$) surfaces have been compared. This may provide a theoretical reference for the experimental study of the NEA GaN ultraviolet photocathode.

*Project supported by the National Natural Science Foundation of China (Grant Nos. 60871012 and 61171042), the Natural Science Foundation of Shandong Province of China (Grant No. ZR2010FL018), and the Higher Educational Science and Technology Program of Shandong Province, China (Grant No. J10LG74).

†Corresponding author. E-mail: bkchang@mail.njust.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

2. Theoretical model and calculation method

All calculations were performed with the quantum mechanics program Cambridge Serial Total Energy Package (CASTEP)[20] and a plane-wave pseudopotential method combined with the generalized gradient approximation (GGA)[21,22] based on density functional theory (DFT). The valence electronic wave function of the primitive cell was expanded using a plane-wave basis set with an energy cutoff of 400 eV. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm was used to relax the structure of the crystal model. The convergence precision was set to an energy change of below 2×10^{-6} eV/atom, a force of less than 0.005 eV/nm, a convergence tolerance of a single atomic energy of below 1×10^{-5} eV/atom, a stress of less than 0.05 GPa, and change in displacement of less than 0.0001 nm in iterative process. The integral in the Brillouin zone was sampled with the Monkhorst–Pack scheme[23] for selected k points with high symmetry. The k points in the Brillouin zone and the plane wave cutoff energy were tested. The number of k points was $9 \times 9 \times 9$ for bulk-phase GaN, and $4 \times 4 \times 1$ for GaN (0001) and GaN (000$\bar{1}$) surfaces. We found these were enough to ensure calculation accuracy. All calculations were carried out in reciprocal space with Ga: $3d^{10}4s^24p^1$, N: $2s^22p^3$, and Cs:$5s^25p^66s^1$ as valence electrons.

The surface slab was modelled with six Ga–N bilayers to simulate GaN (0001) and GaN (000$\bar{1}$) surfaces. Among these bilayers, the top three bilayers were relaxed freely and the bottom three bilayers were fixed at the ideal positions to simulate a bulk environment, and a vacuum thickness of at least 1.5 nm was used to avoid interaction between repeated slabs. The bottom side of the slab was saturated with pseudohydrogen atoms to prevent transfer of surface charges.

3. Results and discussion

Before starting the surface calculations, we first optimized bulk GaN (shown in Fig. 1(a)). The lattice parameters after optimization are given in Table 1. (2×2) GaN (0001) and GaN (000$\bar{1}$) surface models were obtained by cleaving the bulk-phase supercell (shown in Figs. 1(b) and 1(c)).

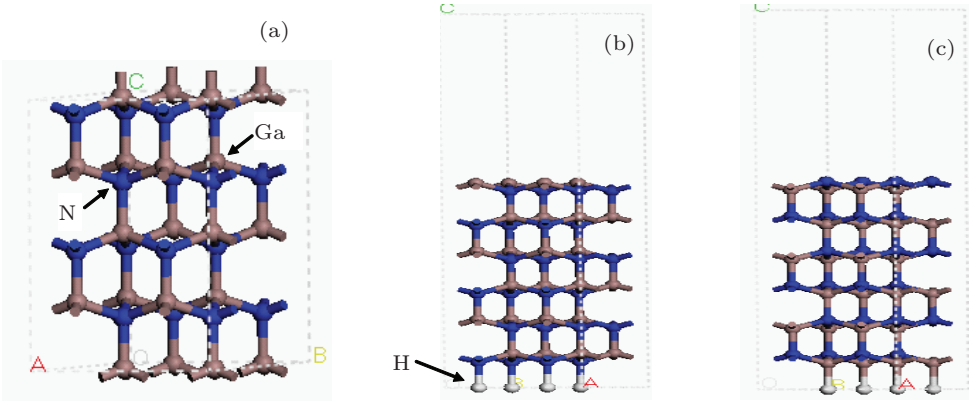


Fig. 1. (colour online) Structure of the GaN supercell: (a) side view of bulk-phase GaN, (b) side view of (2×2) GaN (0001) surface, (c) side view of (2×2) GaN (000$\bar{1}$) surface.

Table 1. Calculated and experimental lattice parameters.

Lattice parameters	a/nm	b/nm	c/nm
This work	0.3225	0.3225	0.5224
Experimental values[23]	0.3189	0.3189	0.5185

The lattice parameters after optimization agree with the experimental values,[24] the error is 0.75% ∼ 1.22%, thereby validating the correctness of the calculation method.

For semiconductors, the work function is the minimum energy needed by electrons at the bottom of the semiconductor to escape externally, and can be expressed as:[25]

$$\Phi = E_{\mathrm{vac}} - E_{\mathrm{f}}, \tag{1}$$

where E_{vac} is the vacuum level, and E_{f} is the Fermi level.

The work function of the GaN (0001) surface calculated by us is 4.2 eV, which is in good agreement with the experimental value of 4.0±0.2 eV,[26] and close to the calculated result of 4.42 eV in Ref. [25], that of the GaN (000$\bar{1}$) surface is 6.667 eV. The dif-

ference between the work functions of the GaN (0001) and GaN (000$\bar{1}$) surfaces is mainly due to the inconsistent direction of the surface dipole. The GaN (0001) surface is more beneficial for the escape of electrons than the GaN (000$\bar{1}$) surface.

4. Adsorption of Cs on GaN (0001) surface

The distance between the first and second bilayers is 0.2023 nm and increases by 2.20%, between the second and third bilayers the distance is 0.1995 nm and increases by 0.81%, compared with an ideal distance of 0.1979 nm between bilayers. The thickness of the first bilayer is 0.0653 nm and condenses by 1.99%, on the second surface is 0.0635 nm and expands by 0.85%, compared with an ideal thickness 0.0647 nm of bilayer.

The adsorption energies $E_{\rm ads}$ of Cs on the GaN (0001) surface is written as[27]

$$E_{\rm ads} = (E_{\rm Cs/GaN(0001)} - E_{\rm GaN(0001)} - nE_{\rm Cs})/n, \quad (2)$$

where n is the number of the adatoms, $E_{\rm GaN(0001)}$ is the total energy of clean GaN (0001) surface, $E_{\rm Cs/GaN(0001)}$ is the total energy of GaN (0001) surface with Cs adatoms, and $E_{\rm Cs} = -548.9466$ eV is the total energy of an isolated Cs atom. If $E_{\rm ads}$ is negative, it means that the absorption process is an exothermic chemical process and is stable. A positive $E_{\rm ads}$ means that the absorption process is endothermic and is unstable.

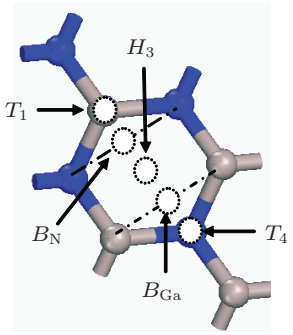


Fig. 2. (colour online) Top view of GaN (0001) surface and the adsorption sites.

The $E_{\rm ads}$ with a Cs adatom on the GaN (0001) surface separately at T_1 (Ga top), H_3 (hollow site), T_4 (N top), $B_{\rm Ga}$ (Ga bridge) and $B_{\rm N}$ (N bridge) sites (shown in Figs. 2 and 3) are -1.89 eV, -2.02 eV, -1.96 eV, -1.98 eV, and -2.04 eV, respectively, and are negative. These results confirm that the adsorption process is stable. $E_{\rm ads}$ is the smallest for a Cs adatom at the T_1 site, and the largest at $B_{\rm N}$ site, and there was little overall difference among the $E_{\rm ads}$ for different adsorption sites. The results show that the adsorption of a Cs atom at $B_{\rm N}$ site is more favorable than the Cs adsorption in other sites.

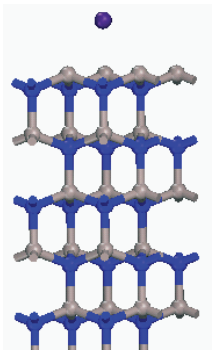


Fig. 3. (colour online) Side view of Cs/GaN (0001) surface.

To study the interaction between Cs atoms and a GaN (0001) surface, $E_{\rm ads}$ of Cs atoms at the $B_{\rm N}$ site with different coverages of 1/4, 1/2, 3/4, and 1 monolayer (ML) were calculated as shown in Fig. 4. As coverage increased, $E_{\rm ads}$ decreased, and the stability of adsorption was reduced. When the coverage of Cs is 3/4 ML, the maximum saturation of Cs atoms is achieved, experimentally proved for a GaN (0001) surface activated by Cs alone.[28] The main reason for this variation is the increased interaction between Cs atoms as coverage increases.

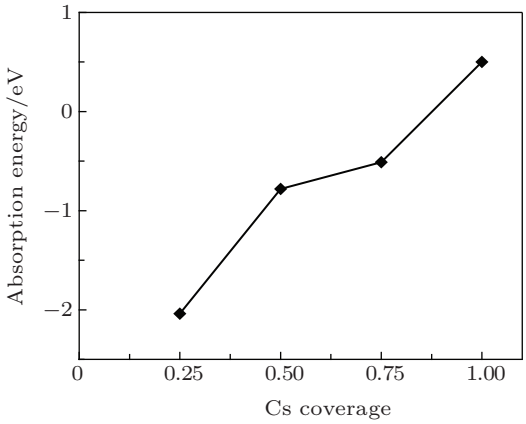


Fig. 4. $E_{\rm ads}$ versus coverage for $B_{\rm N}$ site of GaN (0001) surface.

The change of the work function with a Cs adatom on the surface separately at five high symmetry sites is shown in Table 2. Calculations show that the work function of the GaN (0001) surface reduces after Cs

atom adsorption due to the change of surface dipoles caused by the transfer of Cs 6s electrons to the GaN (0001) surface.

Table 2. Work functions of Cs atoms at high-symmetry sites on GaN (0001) and GaN (000$\bar{1}$) surfaces.

↓ Adsorption system \adsorption sites→	T_1	H_3	T_4	B_{Ga}	B_N
Cs/GaN (0001)[19]	2.38	2.16	2.37	2.36	2.36
Cs/GaN (000$\bar{1}$)	4.20	4.44	4.30	4.30	4.44

In order to investigate the effect of the adsorption of Cs on the work function of the GaN (0001) surface, the work function of Cs atoms at the B_N site with a coverage of 1/4, 2/4, 3/4, and 1 ML were calculated, as shown in Fig. 5. The work function decreases at first, and then rises as coverage increases, and is the smallest when coverage is 2/4 ML, experimentally proved for the GaN (0001) surfaces activated by Cs alone.[29] The main reason for the observed variation is the increased interaction between Cs atoms at high coverage. Some electrons return to Cs atoms from the GaN (0001) surface in order to achieve balance, which decreases the dipole moments between Cs atoms and the GaN (0001) surface, and thus results in an increased work function.

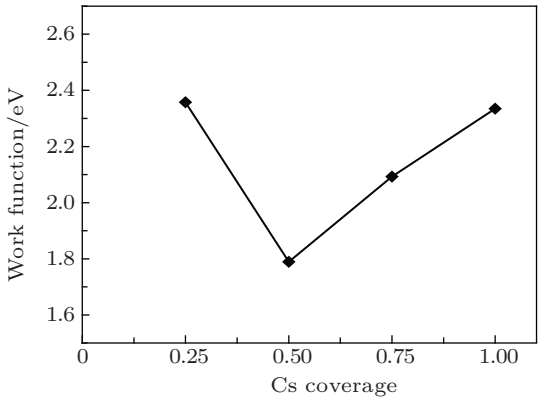


Fig. 5. (colour online) Work function versus coverage for B_N site of GaN (0001) surface.

5. Adsorption of Cs on the GaN (000$\bar{1}$) surface

The distance between the first and second bilayer is 0.2091 nm and increases by 5.67%, between the second and third bilayer the distance is 0.2003 nm and increases by 1.21% after relaxation, compared with that of an ideal distance of 0.1979 nm between bilayers. The thickness of the first bilayer is 0.0351 nm and condenses by 45.78%, that of the second surface bilayer is 0.0576 nm and condenses by 10.97% after relaxation, compared with an ideal thickness of 0.0647 nm. The influence of relaxation on the thickness of the bilayer and the distance between bilayers for the GaN (000$\bar{1}$) surface is larger than that for the GaN (0001) surface. There are larger changes and undulations for the morphology of the GaN (000$\bar{1}$) surface, which indicates that the stability of the GaN (000$\bar{1}$) surface is inferior to that of the GaN (0001) surface. The main reason for the difference between the GaN (0001) and GaN (000$\bar{1}$) surfaces is the different dipole moments in them.

The E_{ads} with a Cs adatom on the GaN (000$\bar{1}$) surface separately at T_1 (Ga top), H_3 (hollow site), T_4 (N top), B_{Ga} (Ga bridge), and B_N (N bridge) positions as shown in Figs. 6 and 7 are −3.59 eV, −3.88 eV, −3.78 eV, −3.73 eV, and −3.79 eV, respectively, and are negative. These results confirm that the absorption process is stable. E_{ads} is the smallest for a Cs adatom at the T_1 site, and the largest for a Cs adatom at the H_3 site. The results show that the most stable adsorption site for Cs on the GaN (000$\bar{1}$) surface is the H_3 site, and E_{ads} of Cs on the GaN (000$\bar{1}$) surface are larger than that of Cs on GaN (0001) surface.

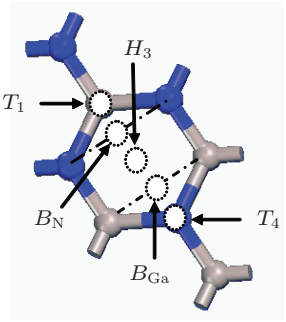


Fig. 6. (colour online) Top view of the GaN (000$\bar{1}$) surface and the adsorption sites.

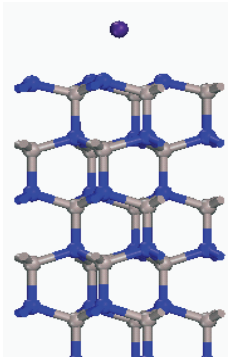


Fig. 7. (colour online) Side view of the Cs/GaN (000$\bar{1}$) surface.

We calculated the E_{ads} of Cs adatoms at the H_3 site with coverage of 1/4, 1/2, 3/4, and 1 ML shown

in Fig. 8. We have found that as coverage is increased, $E_{\rm ads}$ decreases, and the stability of adsorption reduces. When coverage is 1 ML, $E_{\rm ads}$ is negative, and this means that the absorption process is still stable, and saturation of the Cs atoms is not achieved. The main reason for the difference between Cs on GaN (0001) and (000$\bar{1}$) surfaces is the strong electrostatic attraction between the electropositive Cs atoms and electronegative N atoms in the outmost layer of GaN (000$\bar{1}$) surface.

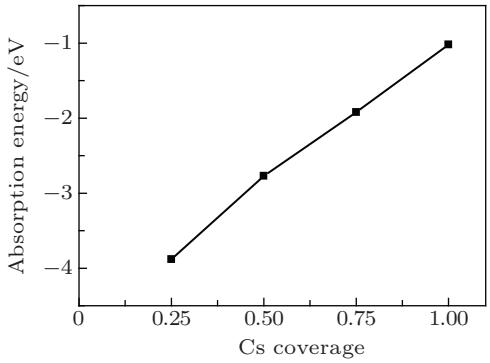


Fig. 8. $E_{\rm ads}$ versus coverage for H_3 site of GaN (000$\bar{1}$) surface.

The work function decreases after the adsorption of Cs on the GaN (000$\bar{1}$) surface, and changes with a Cs adatom on the GaN (000$\bar{1}$) surface at different high symmetry sites separately, shown in Table 2. The main reason that the work function of the GaN (000$\bar{1}$) surface reduces after Cs atom adsorption is that the transfer of Cs 6s electrons to the outermost N atoms leads to the change of surface dipole moment, because the electronegativity of Cs atoms (0.79) is smaller than that of N atoms (3.04).

In order to investigate the effect of the Cs coverage on the work function of the GaN (000$\bar{1}$) surface, the work functions of Cs atoms at H_3 site with coverage of 1/4, 2/4, 3/4, and 1 ML were calculated, as shown in Fig. 9. The results show that as the coverage of Cs atoms rises, work function declines, and the phenomenon of the work function rising observed in the Cs covered GaN (0001) surface does not appear. The main reason is that the $E_{\rm ads}$ of Cs adatoms on the GaN (000$\bar{1}$) surface is larger than that of Cs adatoms on the GaN (0001) surface at the same coverage. The $E_{\rm ads}$ is −1.02 eV when converge is 1 ML, although it decreases with the increase of Cs coverage, and the adsorption is still stable as shown in Fig. 8. At the same time, using Mulliken population analysis, we have found that the outermost N atoms of the GaN (000$\bar{1}$) surface get more electrons with the increase of Cs atom coverage, which makes the dipole moments between the GaN (000$\bar{1}$) surface and the Cs atoms increase, leading to the work function decreasing further, and not bouncing back.

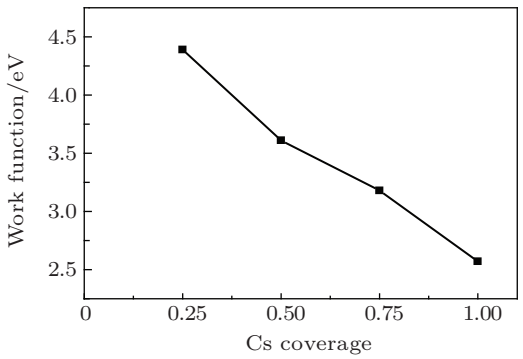


Fig. 9. Work functions versus coverage for the H_3 site of GaN (000$\bar{1}$) surface.

Another find is that a single Cs at the stable adsorption site of the GaN (000$\bar{1}$) surface loses 0.21 e charge more than it does at the stable adsorption site of the GaN (0001) surface, because the electronegativity of Ga atoms (1.81) is smaller than that of N atoms.

6. Conclusion

The stability and work function of the GaN (0001) and GaN (000$\bar{1}$) surfaces were calculated and compared using the first-principles plane-wave ultrasoft pseudopotential method, based on DFT. We have found that the GaN (000$\bar{1}$) surface has worse morphology and a larger undulation than the GaN (0001) surface. The work function of the GaN (000$\bar{1}$) surface is larger than that of the GaN (0001) surface, so The GaN (0001) surface is more beneficial for the escape of electrons than the GaN (000$\bar{1}$) surface under the same conditions. In addition, by researching the adsorption characteristics of Cs on the GaN (0001) and GaN (000$\bar{1}$) surfaces, we can see that the work function decreases after the adsorption of Cs on the GaN surface, the changes of work function and $E_{\rm ads}$ are connected with Cs coverage, but there are large differences in the saturation coverage of Cs atoms and the change of work function between two adsorption systems.

References

[1] Fu X Q, Chang B K, Li B, Wang X H and Qiao J L 2011 *Acta Phys. Sin.* **60** 038503 (in Chinese)

[2] Toru A, Daisuke A, Kohji N and Tomonori I 2010 *Phys. Rev.* B **81** 245317

[3] Li Y H, Pan H H and Xu P S 2005 *Acta Phys. Sin.* **54** 317 (in Chinese)

[4] Bar-Ilan A H, Zamir S, Katz O, Meyler B and Salzman J 2001 *Mater. Sci. Eng.* A **302** 14

[5] Cao Z F, Lin Z J, Lü Y J, Luan C B, Yu Y X, Chen H and Wang Z G 2012 *Chin. Phys.* B **21** 017103

[6] Zhao H P, Liu G Y and Tansu N 2010 *Appl. Phys. Lett.* **97** 131114

[7] Chow W W 2011 *Opt. Express* **19** 21818

[8] Farrell R M, Hsu P S, Haeger D A, Fujito K, DenBaars S P, Speck J S and Nakamura S 2010 *Appl. Phys. Lett.* **96** 231113

[9] Zhang J, Zhao H P and Tansu N 2011 *Appl. Phys. Lett.* **98** 171111

[10] Wang X H, Chang B K, Du Y J and Qiao J L 2011 *Appl. Phys. Lett.* **98** 042102

[11] Wang X H, Chang B K, Ren L and Gao P 2011 *Appl. Phys. Lett.* **98** 082109

[12] Wu C I and Kahn A 1999 *J. Appl. Phys.* **86** 3209

[13] Machuca F, Sun Y, Liu Z, Ioakeimidi K, Pianetta P and Pease R F W 2002 *J. Vac. Sci. Technol.* B **20** 2721

[14] Turnbull A A and Evans G B 1968 *J. Phys.* G: *Nucl. Part. Phys.* **1** 155

[15] Tremsin A S and Siegmund O H W 2005 *Proceedings of SPIE* **5920** 59200I

[16] Maruyama T, Brachmann A, Clendenin J E, Desikan T, Garwin E L, Kirby R E, Luh D A, Turner J and Prepost R 2002 *Nucl. Instrum. Methods Phys. Res.* A **492** 199

[17] Siegmund O, Vallerga J, McPhate J, Malloy J, Tremsin A, Martin A, Ulmer M and Wessels B 2006 *Nucl. Instrum. Methods Phys. Res.* A **567** 89

[18] Du D C, Zhang J C, Ou X X, Wang H, Chen K, Xue J S, Xu S R and Hao Y 2011 *Chin. Phys.* B **20** 037805

[19] Du Y J, Chang B K, Wang X H, Zhang J J, Li B and Fu X Q 2012 *Acta Phys. Sin.* **61** 057102 (in Chinese)

[20] Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys.*: *Condens. Matter* **14** 2717

[21] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048

[22] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[23] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[24] Perlin P, Jauberthie-Carillon C, Itie J P, San Miguel A, Grze-gory I and Polian A 1992 *Phys. Rev.* B **45** 83

[25] Rosa A L and Neugebauer J 2006 *Phys. Rev.* B **73** 205346

[26] Kampen T U, Eyckeler M and MÖnch W 1998 *Appl. Surf. Sci.* **123** 28

[27] González-Hernández R and López-Pérez W 2010 *Phys. Rev.* B **81** 195407

[28] Liu Z, Machuca F and Pianetta P 2004 *Appl. Phys. Lett.* **85** 1541

[29] Benemanskaya G V, Vikhnin V S, Shmidt N M, Frank-Kamenetskaya G E and Afanasiev I V 2004 *Appl. Phys. Lett.* **85** 1365