



## Surface Science Letters

## Variation in anisotropic dispersion relations of self-assembled monolayer on Cu(001) induced by modulation of molecular structures

Ken Kanazawa<sup>a</sup>, Miki Nakamura<sup>a</sup>, Hui Huang<sup>b</sup>, Atsushi Taninaka<sup>a</sup>, Hidemi Shigekawa<sup>a,\*</sup><sup>a</sup> Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8573, Japan<sup>b</sup> Hefei University, China

## ARTICLE INFO

## Article history:

Received 19 May 2014

Accepted 16 July 2014

Available online 31 July 2014

## Keywords:

Scanning tunneling microscopy

Anisotropic dispersion relation

 $\beta$ -Alanine

Amino acid

2DEG

Cu(001)

## ABSTRACT

The two-dimensional electron gas (2DEG) states formed by self-assembled monolayers (SAM) of  $\beta$ -alanine molecules on a Cu(001) surface showed anisotropic dispersion relations different from those formed by glycine SAM.  $\beta$ -Alanine has a structure with an additional methylene group compared with glycine, and enantiomeric isomers were formed through adsorption, similarly to glycine. The anisotropic ratio of the effective masses was changed from 10 for glycine to 3.6 for  $\beta$ -alanine, suggesting the possibility of manipulating electronic structures by modification of the molecular structures. Although the growth modes were different for  $\beta$ -alanine and glycine, 2DEG states with standing waves were observed only for the  $p(2 \times 4)$  phase in both cases, suggesting a key role of the interactions in the arrangement of this phase, together with the importance of the enantiomeric isomers formed through adsorption, which is also a characteristic of both molecules.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

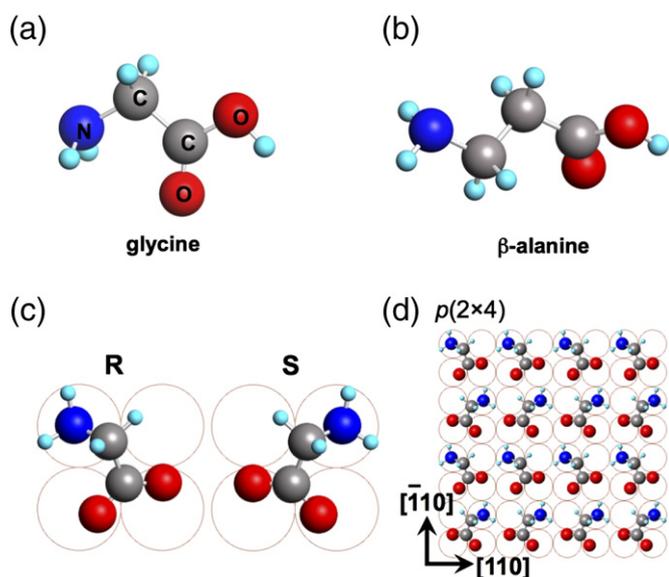
The control of low-dimensional electronic structures has been a key factor in the development of electronic devices. The modulation of free-electron-like states arising in organic thin film/metal interfaces has been attracting considerable attention because of its potential for further device applications as well as its basic importance for understanding fundamental mechanisms in molecular electronics [1–11]. The quantum confinement of surface electrons is an interesting research target, and various types of molecules have been used to produce quantum corrals with different shapes and sizes [1–6]. On the other hand, the two-dimensional electron gas (2DEG) states associated with a self-assembled monolayer (SAM) of molecules on a metal surface are also the area of study attracting interest [7–11]. Recent scanning tunneling microscopy/spectroscopy (STM/STS) studies have revealed the formation of free-electron-like structures, for example, in the SAMs of 3,3,9,10-perylenetetracarboxylic-acid-dianhydride molecules on Ag(111) [7] and glycine molecules on Cu(001) [8]. In the glycine/Cu(001) structure, a dispersion relation with tenfold anisotropy, which is different from the symmetry of the substrate, was observed [8]. Exploring the possibility of manipulating such 2DEG structures is desirable for advancing the development of molecular electronic devices.

In this paper, we present the first results for the variation in the anisotropic dispersion relations in SAMs on a Cu(001) surface induced by the modulation of molecular structures.

$\beta$ -Alanine was chosen as the sample because of its characteristic property of chirality similar to that of glycine. Among the  $\alpha$ -amino acids, glycine is the only molecule that does not have chirality (Fig. 1(a)). However, enantiomeric isomers of glycine appear on a Cu surface through the dissociation of hydrogen, depending on the directional relationship of the two groups in the adsorbed form as schematically illustrated in Fig. 1(c) [12]. Two different structures,  $p(2 \times 4)$  and  $c(2 \times 4)$ , are formed with different arrangements of the isomers, i.e., the two isomers are alternately ordered for the  $p(2 \times 4)$  phase (Fig. 1(d)), while the  $c(2 \times 4)$  phase consists of only one type (Fig. 1 in ref. [13]). The 2D electronic structure with tenfold anisotropy of effective mass was observed only for the  $p(2 \times 4)$  phase, suggesting the importance of this arrangement.

Alanine has two isomers, i.e.,  $\alpha$ - and  $\beta$ -alanine.  $\alpha$ -Alanine naturally has R- or S-chirality (D- or L-alanine), while  $\beta$ -alanine has a structure with an additional methylene group ( $-\text{CH}_2-$ ) in its main chain compared with glycine and does not have chirality, as shown in Fig. 1(b). In the case of  $\alpha$ -alanine, even molecules with both chiralities are adsorbed together, only  $c(2 \times 4)$  domains consisting of D- or L-alanine are separately grown, and the  $p(2 \times 4)$  phase, which consists of the molecules with two isomers and has a 2DEG structure in the case of glycine, is not formed [13–15]. This result suggests the importance of the process of producing enantiomeric isomers through adsorption on a Cu(001) surface, as illustrated for the case of glycine. Namely, if  $\beta$ -alanine molecules produce enantiomeric isomers through adsorption similar to the case of glycine, the formation

\* Corresponding author. Tel./fax: +29 853 5276.  
E-mail address: [hidemi@ims.tsukuba.ac.jp](mailto:hidemi@ims.tsukuba.ac.jp) (H. Shigekawa).  
URL: <http://dora.bk.tsukuba.ac.jp> (H. Shigekawa).



**Fig. 1.** Schematic structures of (a) glycine and (b)  $\beta$ -alanine molecular structures, (c) chirality of glycine molecule produced by adsorption on a Cu(001) surface, and (d) molecular arrangement of the  $p(2 \times 4)$  phase.

of the  $p(2 \times 4)$  phase and the production of 2DEG states may be realized. Furthermore, the existence of a methylene group may modify the electronic structure.

## 2. Materials and methods

A clean Cu(001) surface was prepared by three cycles of  $\text{Ar}^+$  ion bombardment and annealing at 820 K. After  $\beta$ -alanine source was outgassed by heating the  $\text{Al}_2\text{O}_3$  crucible at 330 K for 5 h,  $\beta$ -alanine

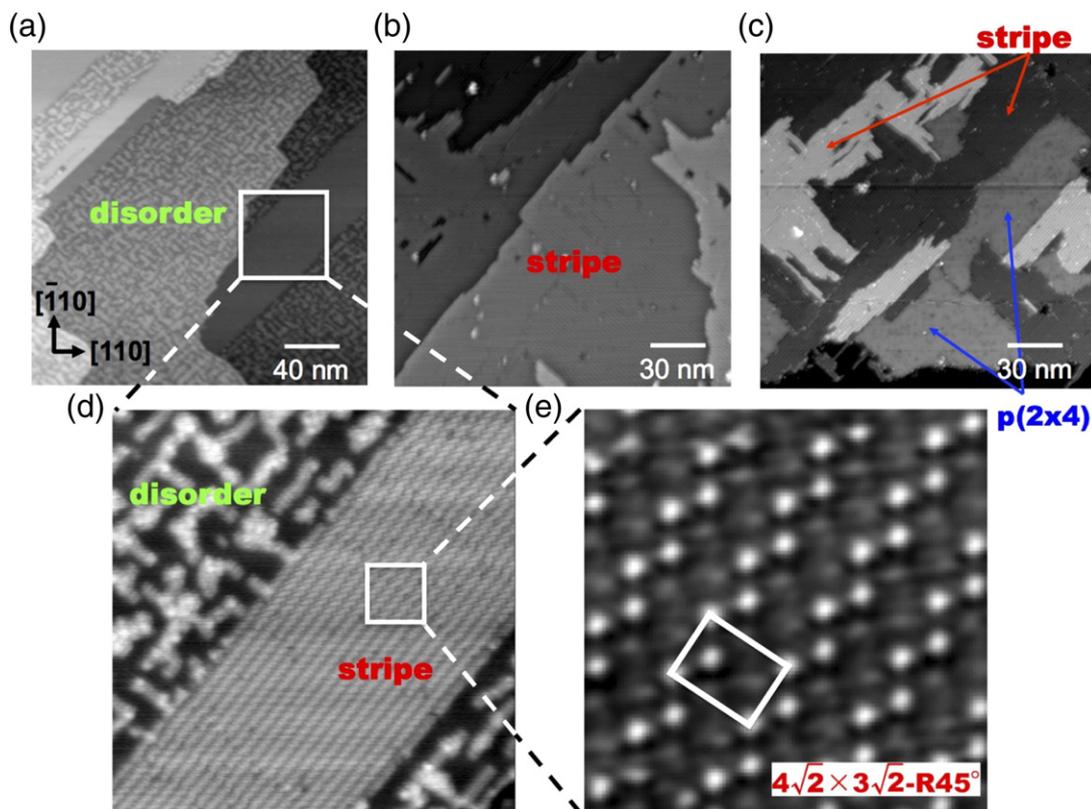
molecules were adsorbed on the substrate where the source and Cu sample temperatures were maintained at 370 K and room temperature (RT), respectively. Then STM/STS measurements were performed at 5 K using a tungsten tip.

## 3. Results and discussion

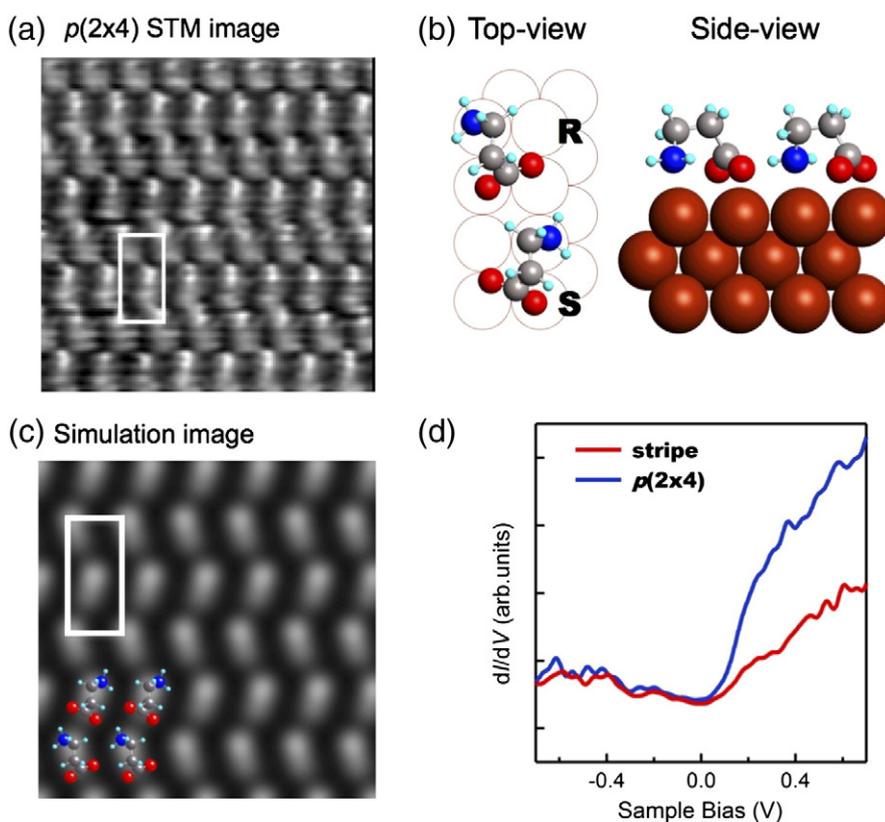
Fig. 2 (a) to (c) shows STM images obtained in the growth process of a  $\beta$ -alanine molecular SAM on a Cu(001) substrate. Three structures were observed in the growth step with increasing amount of adsorbed molecules: (1) a disordered phase, (2) a stripe phase and (3) a  $p(2 \times 4)$  phase. With increasing amount of adsorption, the disordered phase appeared first, and then the stripe phase emerged (Fig. 2(a)). After the stripe phase covered the surface (Fig. 2(b)), the  $p(2 \times 4)$  phase, which was observed for glycine, was formed (Fig. 2(c)).

Fig. 2 (d) and (e) shows magnified STM images of the (a) disordered phase and (b) stripe phase. In the disordered phase,  $\beta$ -alanine molecules tended to form linear structures in the  $[010]$  and  $[100]$  directions. The stripe phase appears to be linearly ordered in the  $[010]$  direction as shown in Fig. 2 (d); however, this is due to the alternate variations in contrast as shown in the magnified image (Fig. 2(e)). The high-resolution image shows that the stripe phase is formed by a  $4\sqrt{2} \times 3\sqrt{2}$ -R45° structure.

Fig. 3 (a) shows a magnified STM image of the  $p(2 \times 4)$ . Although it is difficult to determine the detailed structures from the STM image because the characteristics of the molecular images are less clear than those of the case of glycine [8], the structural model was considered by assuming arrangement similar to that of glycine shown in Fig. 1 (d). To examine the structure, we carried out a simple density functional theory calculation using the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) with the ABINIT code with plane-wave-based norm-conserving pseudopotentials [16,17]. The  $(2 \times 4 \times 4)$  supercell including the slab model with three Cu(001) layers and two  $\beta$ -alanines



**Fig. 2.** STM images of  $\beta$ -alanine molecular structures with increasing the amount of adsorbed molecules ((a)  $V_s = -250$  mV,  $I_t = -1$  nA, (b)  $V_s = -350$  mV,  $I_t = -1$  nA, (c)  $V_s = 350$  mV,  $I_t = 0.3$  nA). Magnified STM images of (d) disordered and (e) stripe structures (thermal drift, corrected).

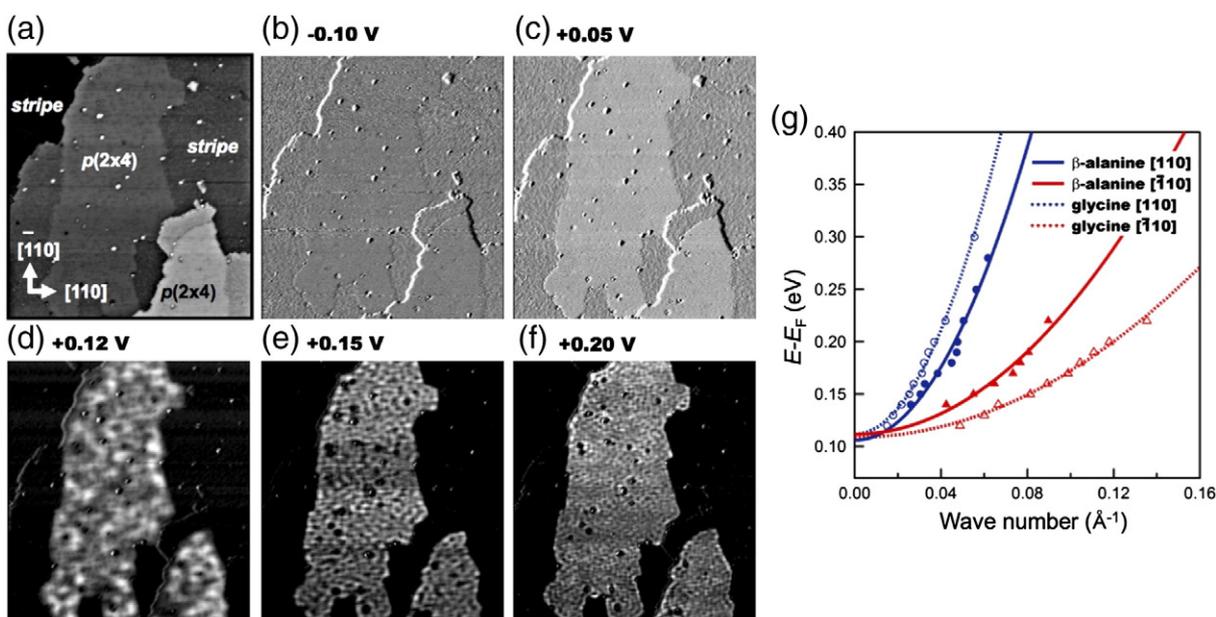


**Fig. 3.** (a) Magnified image of the  $p(2 \times 4)$  structure in Fig. 2 ( $V_s = -300$  mV,  $I_t = -1$  nA). (b) Schematic of slab models used for calculation. (c) Simulated image calculated using the molecular structure shown in (b). (d)  $dI/dV$  curves obtained for a bare Cu surface and above the stripe and  $p(2 \times 4)$  structures.

shown in Fig. 3 (b) was used for the calculation. The energy cutoff of the calculation was 60 Ry. The  $k$ -point meshes of  $4 \times 4 \times 1$  were used for the calculations. From the spatial distribution of the local density of states (LDOS) near the Fermi energy  $E_F$  in the surface region ( $E_F - 0.5$  eV  $< E < E_F$ ), we obtained the result shown in Fig. 3 (c), which is comparable to the STM image shown in Fig. 3 (a) [18]. The agreement of the experimental and simulated images is good, indicating the validity of the structural model for the  $p(2 \times 4)$  phase. Namely, although the growth

mode of  $\beta$ -alanine is different from that of glycine [13], a  $p(2 \times 4)$  phase with the molecular arrangement similar to that of glycine is formed.

Next, we investigated the electronic structure of the  $p(2 \times 4)$  phase. Fig. 3 (d) shows  $dI/dV$  curves measured above the stripe and  $p(2 \times 4)$  phases. The  $p(2 \times 4)$  phase exhibits a step-like shape, suggesting the existence of a 2DEG structure similar to that appearing in the case of glycine molecules [8]. To examine the origin of this signal, we measured



**Fig. 4.** (a) Topographic image and (b) to (f) typical  $dI/dV$  images obtained over the area in (a). (g) Dispersion relations obtained from the bias dependence of the wavelength in the  $dI/dV$  images. The results obtained for the case of glycine in a previous paper [8] are also shown.

**Table 1**

Values of effective masses  $m^*$  in the [110] and  $\bar{1}\bar{1}0$  directions ( $m_e$ : electron mass) and the energy minima  $E_0$  of the dispersion relations obtained for  $\beta$ -alanine and glycine [8].

	Glycine	$\beta$ -Alanine
$m^*_{[110]}/m_e$	$6.1 \times 10^{-2}$	$8.7 \times 10^{-2}$
$m^*_{\bar{1}\bar{1}0}/m_e$	$6.1 \times 10^{-1}$	$3.1 \times 10^{-1}$
$E_0(\text{meV})$	$\sim 110$	

the  $dI/dV$  images. Fig. 4 shows (a) the topographic image and (b) to (f)  $dI/dV$  images obtained over the area in (a) (lock-in modulation = 8 mV, frequency = 2.74 kHz, scan speed = 2 ms/pixel,  $512 \times 512$  pixels). The modulated LDOS of the 2DEG were clearly observed as expected, which are similar to the case of glycine [8]. From the bias dependence of the autocorrelations of the modulated LDOS, nearly free-electron-like dispersion relations were obtained, which is shown in Fig. 4 (g) together with the results obtained for glycine in the previous work.

The effective masses obtained for  $\beta$ -alanine are  $8.7 \times 10^{-2} m_e$  and  $3.1 \times 10^{-1} m_e$  ( $m_e$ : electron mass) for the [110] and  $\bar{1}\bar{1}0$  directions, which are more isotropic than those obtained for glycine,  $6.1 \times 10^{-2} m_e$  and  $6.1 \times 10^{-1} m_e$  for the [110] and  $\bar{1}\bar{1}0$  directions, respectively. The same value of the energy minimum  $E_0$  in both cases is considered to be due to the fact that the methylene group does not shift the energy level markedly, probably because of its electroneutrality. The obtained values are summarized in Table 1.

The tenfold difference in the effective masses for the case of glycine is attributed to the anisotropy of the molecular interactions in the SAM; that is, the interaction along the molecular rows in the [110] direction is stronger than that between the molecular rows. In fact, the  $p(2 \times 4)$  arrangement exhibited some phase defects formed by the substitution of a molecular row of one chirality with a molecular row of the other chirality. This is likely to be because of the larger overlap of electronic states in molecules along the [110] direction, originating from the carboxyl or amino groups in the molecules (Fig. 1(d)).

In consideration of the similar  $p(2 \times 4)$  arrangement for both molecules, shown in Figs. 1 (d) and 3 (c), the rather isotropic electronic structure realized by  $\beta$ -alanine may be a result of the effects of the direct modification of intramolecular orbitals and strain, which may induce the atomic displacement of the amino and carboxylate groups from the case of glycine, caused by the additional methylene group in the  $\beta$ -alanine molecule. To obtain a further understanding, however, more detailed analysis of the molecular interactions is necessary, which is left for a future study.

#### 4. Conclusions

In conclusion, the possibility of manipulating the dispersion relations of 2DEG structures formed in a SAM/metal interface was

attempted by comparing the electronic structures obtained using  $\beta$ -alanine molecules and glycine molecules. Although the only difference between the structures of  $\beta$ -alanine and glycine is an additional methylene group ( $-\text{CH}_2-$ ) in  $\beta$ -alanine, the anisotropic ratio of the effective masses was successfully changed from 10 for glycine to 3.6 for alanine. Although a three-step growth process was observed for  $\beta$ -alanine, 2DEG states were only produced for the  $p(2 \times 4)$  phase, similar to the case of glycine, suggesting a key role of the interactions in the arrangement of this phase, together with the importance of the enantiomeric isomers appearing through adsorption on the Cu surface, observed for both molecules. The manipulation of anisotropy in free-electron-like 2DEG states by the modification of the molecular structures to provide additional functions may be a possible means of further developing future molecular devices.

#### Acknowledgments

Support from Japan Society for the Promotion of Science (Grants-in-Aid for Scientific Research) is acknowledged.

#### References

- [1] Y. Pennec, W. Auwärter, A. Schiffrin, A. Weber-Bargioni, A. Riemann, J.V. Barth, Nat. Nanotechnol. 2 (2007) 99.
- [2] C.R. Moon, L.S. Mattos, B.K. Foster, G. Zeltzer, H.C. Manoharan, Nat. Nanotechnol. 4 (2009) 167.
- [3] F. Klappenberger, D. Kühne, W. Krenner, I. Silanes, A. Arnau, F.J. García de Abajo, S. Klyatskaya, M. Ruben, J.V. Barth, Nano Lett. 9 (2009) 3509.
- [4] J. Lobo-Checa, M. Matena, K. Müller, J.H. Dil, F. Meier, L.H. Gade, T.A. Jung, M. Stöhr, Science 325 (2009) 300.
- [5] F. Klappenberger, D. Kühne, W. Krenner, I. Silanes, A. Arnau, F.J. García de Abajo, S. Klyatskaya, M. Ruben, J.V. Barth, Phys. Rev. Lett. 106 (2011) 11312.
- [6] K. Kanazawa, A. Taninaka, H. Huang, M. Nishimura, S. Yoshida, O. Takeuchi, H. Shigekawa, Chem. Commun. 47 (2011) 11312.
- [7] R. Temirov, S. Soubatch, A. Lucian, F.S. Tautz, Nature (London) 444 (2006) 350.
- [8] K. Kanazawa, Y. Sainoo, Y. Konishi, S. Yoshida, A. Taninaka, A. Okada, M. Berthe, N. Kobayashi, O. Takeuchi, H. Shigekawa, J. Am. Chem. Soc. 129 (2007) 740.
- [9] L. Chen, H. Li, A.T.S. Wee, Nano Lett. 9 (2009) 4292.
- [10] N. Gonzalez-Lakunza, I. Fernández-Torrente, K.J. Franke, N. Lorente, A. Arnau, J.I. Pascual, Phys. Rev. Lett. 100 (2008) 156805.
- [11] B.W. Heinrich, L. Limot, M.V. Rastei, C. Iacovita, J.P. Bucher, D.M. Djimbi, C. Massobrio, M. Boero, Phys. Rev. Lett. 107 (2011) 216801.
- [12] V. Efsthathiou, D.P. Woodruff, Surf. Sci. 531 (2003) 304.
- [13] K. Kanazawa, A. Taninaka, O. Takeuchi, H. Shigekawa, Phys. Rev. Lett. 99 (2007) 216102.
- [14] X. Zhao, R.G. Zhao, W.S. Yang, Surf. Sci. 442 (1999) L995.
- [15] H. Iwai, C. Egawa, Langmuir 26 (2010) 2294.
- [16] X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, D.C. Allan, Comput. Mater. Sci. 25 (2002) 478.
- [17] X. Gonze, G.-M. Rignanese, M. Verstraete, J.-M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, Ph. Ghosez, M. Veithen, J.-Y. Raty, V. Olevano, F. Bruneval, L. Reining, R. Godby, G. Onida, D.R. Hamann, D.C. Allan, Z. Kristallogr. 220 (2005) 558.
- [18] J. Tersoff, D.R. Hamann, Phys. Rev. Lett. 50 (1983) 1998.